İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THE INFLUENCE OF DIFFERENT WATER-TO-CEMENT RATIOS ON COMPRESSIVE STRENGTH OF FLY ASH-ADDED CONCRETES

M.Sc. Thesis by
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DEĞİŞİK SU-ÇİMENTO ORANLARININ UÇUCU KÜLLÜ BETONLARIN BASINÇ DAYANIMINA ETKİSİ

YÜKSEK LİSANS TEZİ

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FOREWORD

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ABBREVIATIONS

CSH **:** Calcium Silicate Hydrate
CaO **:** Calcium oxyde
$Ca(OH)_2$ **:** Calcium hydroxide
ASTM **:** American Society for Testing and Materials

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THE INFLUENCE OF DIFFERENT WATER TO CEMENT RATIOS ON THE STRENGTH OF FLY ASH ADDED CONCRETES

SUMMARY

In this study, the relation between fly ash added concretes and different water to cement ratios is invastigated. Fly ash is a mineral admixture used to improve the properties of Fly ash is used, as mineral admixture material in concrete. Many chemical and mineral admixtures are used to increase the compression strength of concrete, for its being natural and industrial waste, fly ash is considered to be one of the puzzolans to be invastigated and studied for the concrete industry. As industrial waste, it can risk the environmental cleaning in case it is left to atmosphere, so using it in concrete as admixture is one of environmental friendly applications, moreover, it is known that fly ash reduces the amount of CO_2 being released to the atmosphere as a result of the reactions in concrete. In this research, the behavior of fly ash added concretes is investigated. Two types of fly ash were used, high lime conctent fly ash (C class) and low lime content fly ash (F class). To compare the obtained results and evaluate them precisely, a third group of fly ash free concrete was produced to control the changes in compression stregnth and the alkalinity of fly ash added concretes, six different water-to-binder ratios were used. However, to measure the pH of the specimens two methods of measurements were applied, powder solution method and extracted pore solution method, High Pressure Pore solution extraction device was used in this method. The tests were performed for three different ages (7 days, 28 days and 90 days).

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ÖZET

Uçucu küller, yıllardır inşaat ve yapı sektöründe, betonlarda katkı maddesi olarak kullanılmıştır. Beton dayanımını arttırmak için, çok sayıda kimyasal ve mineral katkı maddesi kullanılmaktadir. Doğallığı ve endüstriyel atık olması açısından, uçucu küllerin, diğer puzolanlardan, betonda kullanılmasının daha çok farklı kılan ve detaylı araştırılması gerektiren bir özelliktir, sanayi atık olması sebebiyle atmosfere bırakılması halinde hava kirliliğine yol açar, bu yüzden betonda katkı maddesi olarak kullanılması çevre dostu bir uygulama olduğu görülür, ayrıca betondaki reaksyonlardan çıkan CO_2'in miktarını azalttığı da biliniyor. iki tip uçucu kül, yüksek kireç içerikli uçucu kül (C sınıfı) ve düşük kireç içerikli uçucu kül (F sınıfı) kullanılmıştır. uçucu küllü betondan elde edilen sonuçları karşılaştırmak ve tam basınç dayanımı ve alkalinitesindeki değişiklikleri kontrol etmek ve değerlendirmek için külsüz betondan üçüncü bir grup daha üretilmiştir, altı farklı su-bağlayıcı oranları kullanılmıştır. Ayrıca, numunelerin pH'ini ölçmek için iki yöntem uygulanmıştır, beton tozu çözeltisi yöntemi ve çıkarılmış boşluk suyu yöntemi. Betonun boşluk suyunu elde etmek için, Yüksek Basınçlı Boşluk suyu çıkarma cihazı, diye özel bir alet kullanılmıştır, çok yüksek basınç altında numuneden sıkıldan boşluk suyunun pH'i ölçülür Testler (7 gün, 28 gün ve 90 gün) üç farklı yaş için yapıldı.

1. INTRODUCTION

1.1 Historical Notes

Construction materials were always the most essential need for humans. The need of safe, strong and protective shelter was one of the necessities that led human to search for suitable and convenient materials to construct the needed shelter. After ages of progress and civilization the needs changed and became luxuries not only necessities, so according to those changes the demand of new materials start to appear so man started to look for materials for decoration and art. The increase of luxury needs and variation of construction purposes forced us to find new sources of building materials to provide us with the proper material.

The good construction material must be strong, durable, convenient for use and not expensive. Lime is one of the most important material in construction, as it was discovered in the very old days of human history. It needs some operations to get it ready to be in use, calcining calcium carbonate produces a material called quicklime, CaO, and in water it hydrates to give slaked lime, $Ca(OH)_2$, the ancient people used slaked lime for plaster [1]. The ancient Egyptians used it in lime plaster and decorated it by coloured pigments. Lime was first used by the Greeks and Romans, as a cementitious material [1]. Although they knew some applications of limestone specially in developing the hydraulic properties, their chemical information was not enough to explain many phenomena about limestone. The Romans defined the best lime as, the lime which is produce by white or light coloured limestone [1]. The knowledge about limestone stayed incomplete and not chemically detailed, till the 18^{th} century when John Smeaton started to investigate limestone chemically [1]. In 1824 Joseph Aspdin discovered a new cementitious material lately called portland cement.

He explained the way he discovered this material and said:" I obtained the limestone itself, and I cause the puddle or powder or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labour or machinery. After the proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan till the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic is entirely expelled. The mixture so calcined is to be ground, beat or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into the consistency of mortar, and thus applied to the purposes wanted."[1]

1.2 Cement production

The main elements, that cement production depends on, are lime and silica. production of cement starts by obtaining raw materials like, limestone, shells or chalk, shale, clay, sand and iron ore. As the transportation of raw material to the production site is more difficult than transportation of cement to the distribution centres, production sites are constructed close to the quarry to make the transportation of raw material easier and less in cost. There are two types of production processes [2].

1.2.1 Wet Process

In this process raw materials generally are wet. Therefore, those materials are proportioned to the main contents of cements, and then they are crashed to powder by the cylindrical mill. The powder is mixed with water to form slurry, and then the slurry passes from the kiln. As the slurry has more than 40% of water, it is needed to get rid of this amount of water by evaporating. The slurry is heated up to 1450 C. [2]

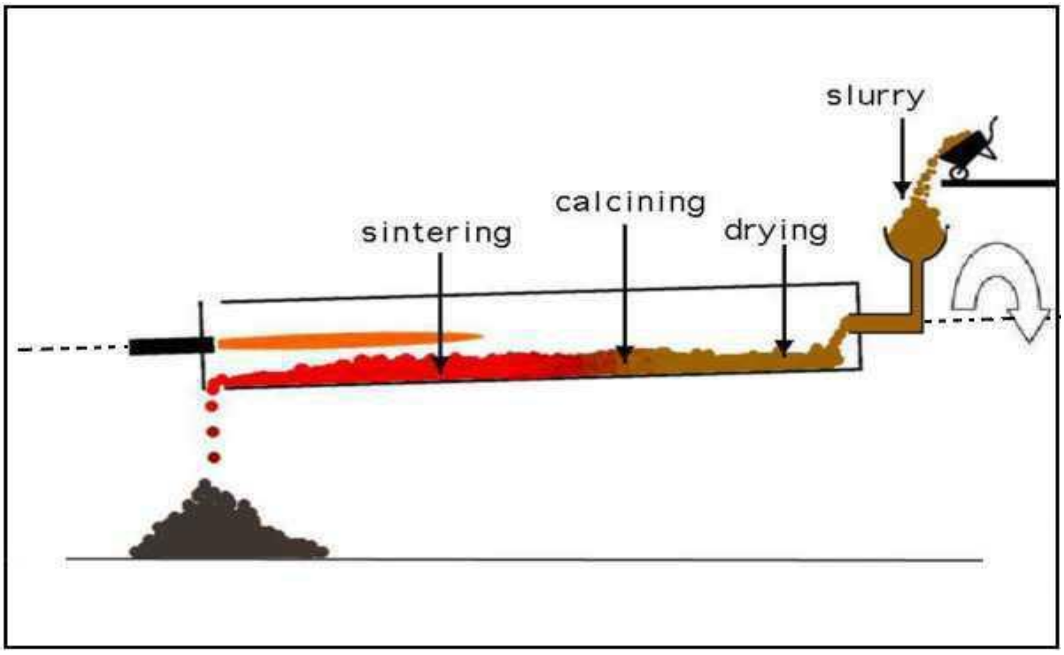

Figure 1-1: Schematic diagram of wet process [3].

In the above shape, the way of raw material in the kiln, is seen. After leaving the raw material to the upper hole of the kiln it passes from cylindrical mill (body of the kiln), first stage is drying as the slurry consists of 40% of water [2]. Then calcining comes after, as it is burning the material and getting it decarbonised, to reach the last stage which is sintering so at the end of the kiln the material comes out as small balls. The product is cooled then crashed to get the fine material of the cement. Gypsum is added at the end o the process to control the setting.

1.2.2 Dry Process

Dry process is similar to the wet process but in dry process the material is not wet so there is no need to dry the material in the kiln. In the last years, production of cementdepends on dry process, because it saves more energy as there is no drying stage.

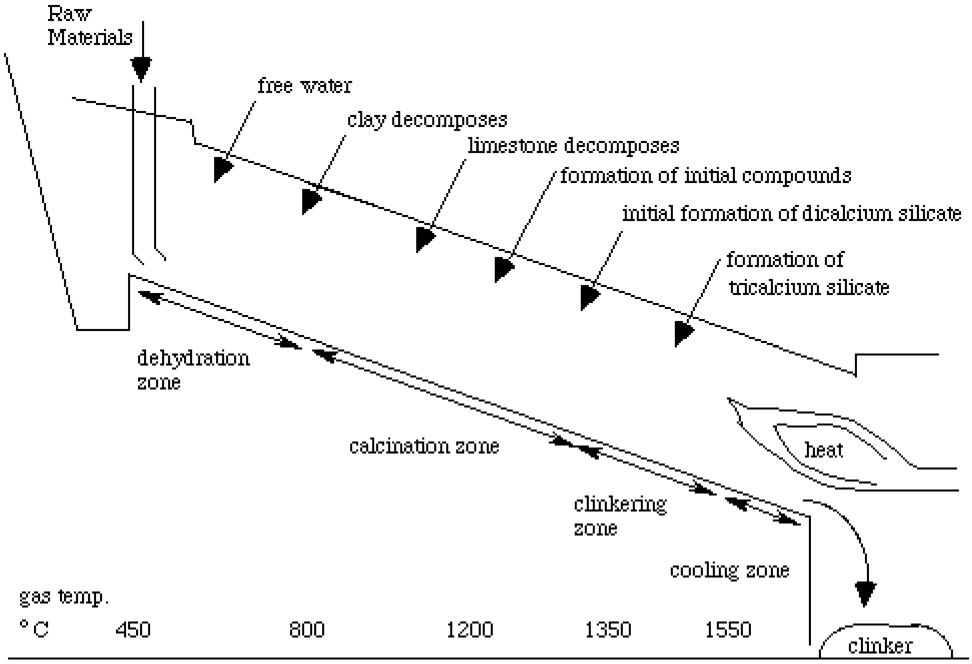

Figure 1-2: Schematic diagram of cement production process in the kiln [4]

1.2.3 Components of Portland Cement

ASTM C 150 defines portland cement as "hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition." Clinkers are nodules (diameters, 0.2-1.0 inch [5-25 mm]) of a sintered material that is produced when a raw mixture of predetermined composition is heated to high temperature. The low cost and widespread availability of the limestone, shales, and other naturally occurring materials make portland cement one of the lowest-cost materials widely used over the last century throughout the world. Concrete becomes one of the most versatile construction materials available in the world [5].

Table 1-1: Portland cement types and its uses

Cement type	Use
I[1]	General purpose cement, when there are no extenuating conditions
II[2]	Aids in providing moderate resistance to sulfate attack
III	When high-early strength is required
IV[3]	When a low heat of hydration is desired (in massive structures)
V[4]	When high sulfate resistance is required
IA[4]	A type I cement containing an integral air-entraining agent
IIA[4]	A type II cement containing an integral air-entraining agent
IIIA[4]	A type III cement containing an integral air-entraining agent

There are four main components of Portland cement, and they are:

C_3S : tricalcium silicate

C_2S : dicalcium silicate

C_3A : tricalcium aluminate

C_4AF : tetracalcium aluminoferrite

1.3 Concrete

Concrete is the most widely used building material. It is rock like material consists of cement as binder or any cementitious material such as: fly ash slag cement, aggregates such as gravels or crushed rocks as coarse aggregates and sand as fine aggregates, and in some cases chemical admixtures can be used. To combine those integrants together water is needed. Hardened concrete comes after mixing the mentioned elements together with water.

1.3.1 Hydration

In concrete, cement is the main binder so it is the reactive material that reacts with water. The reaction of cement components with water is called hydration. Tricalcium silicate and dicalcium silicate form about 75-80% of cement contents, as shown in the table below [6].

Table 1-2: Composition of portland cement with chemical composition and weight percent.

Cement Compound	Weight Percentage	Chemical Formula
Tricalcium silicate	50 %	Ca_3SiO_5 or $3CaO \cdot SiO_2$
Dicalcium silicate	25 %	Ca_2SiO_4 or $2CaO \cdot SiO_2$
Tricalcium aluminate	10 %	$Ca_3Al_2O_6$ or $3CaO \cdot Al_2O_3$
Tetracalcium aluminoferrite	10 %	$Ca_4Al_2Fe_2O_{10}$ or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
Gypsum	5 %	$CaSO_4 \cdot 2H_2O$

According to the information in the table above, it is considered that the most important reactions in the hydration are the reaction of tricalcium silicate with water and the reaction of dicalcium silicate with water.

Tricalcium silicate + Water $\longrightarrow$ Calcium silicate hydrate+Calcium hydroxide + heat

$2\ Ca_3SiO_4 + 7\ H_2O \longrightarrow 3\ CaO{\cdot}2SiO_2{\cdot}4H_2O + 3\ Ca(OH)_2 + 173.6kJ$

Or in abbreviation

$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH$

In this reaction, tricalcium silicate rapidly reacts with water releasing calcium ions, hydroxide ions, and a large amount of heat. The release of alkaline hydroxide (OH^-) ions results in a quick rise of pH to over 12 [6].

The reaction slowly continues producing calcium and hydroxide ions until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Ions precipitate out of solution accelerating the reaction of tricalcium silicate to calcium and hydroxide ions. (Le Chatlier's principle). The evolution of heat is then increased [6].

The next reaction is the reaction of dicalcium silicate with water:

Dicalcium silicate + Water $\longrightarrow$ Calcium silicate hydrate + Calcium hydroxide +heat

$2\ Ca_2SiO_4 + 5\ H_2O \longrightarrow 3\ CaO{\cdot}2SiO_2{\cdot}4H_2O + Ca(OH)_2 + 58.6\ kJ$

Or in abbreviation

$2C_2S + 5H \longrightarrow C_3S_2H_3 + CH$

The reaction of dicalcium silicate effects the strength of concrete in the later ages. Being less reactive, dicalcium silicates react with waqter very slowly [6].

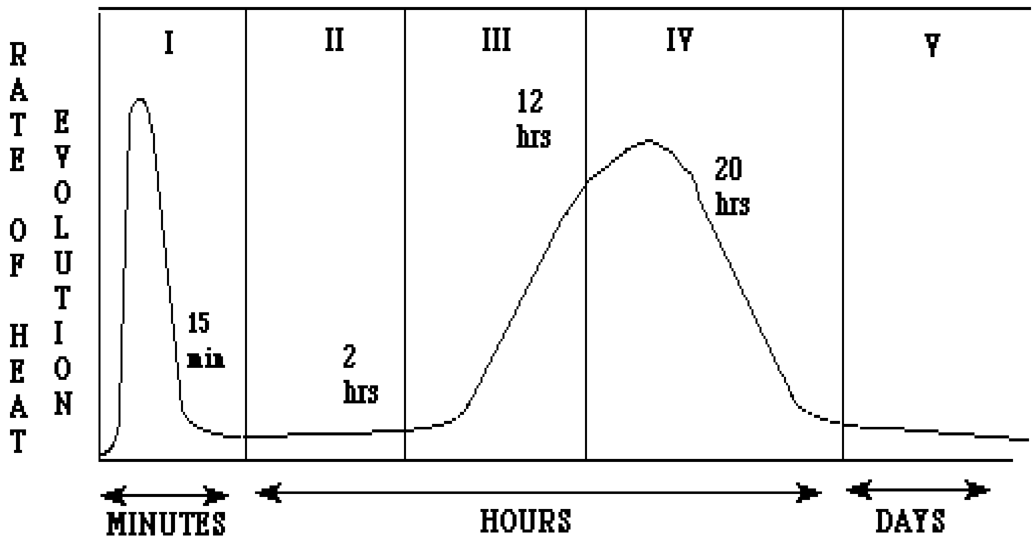

Figure 1-3: Rate of heat evolution during the hydration

In the figure above, stage I shows the rapid increase of the heat in the early few minutes when tricalcium silicates enters the reaction with water, then it goes down for some about three hours (II) when the water is prevented to reach unhydrated parts, then the hydration sarts again in stage III to reach the peak point in IV after 20 hours and that is because of the beginning of dicalcium silicates to be hydrated.

1.3.2 Factors Affecting The Strength of Concrete

There are many factors affecting the strength of concrete, some of them will be mentioned in this reserach such as, the characteristics of cement, the age, mixing rate, curing and admixtures. Those factors will be discussed in details in this session.

Characteristics of cement are very important in determining the strength of concrete. By changing the tricalcium silicates (Ca_3SiO_5) content, the properties of concrete will change as tricalcium siliscates is a major content in the process of hydration. Incresing the fineness of the paticles of cement can be a factor to improve the strength of concrete [7].

Age of concrete is a determinant factor in affecting the strength. Concrete gains its main part of strength in the early ages, but in concretes that have more dicalcium silicates the increase of the strength is not so rapid and comes slowly [7]. In general, concrete gains most of its stregnth from the first week to the fourth week, or between 7 days age and 28 days age.

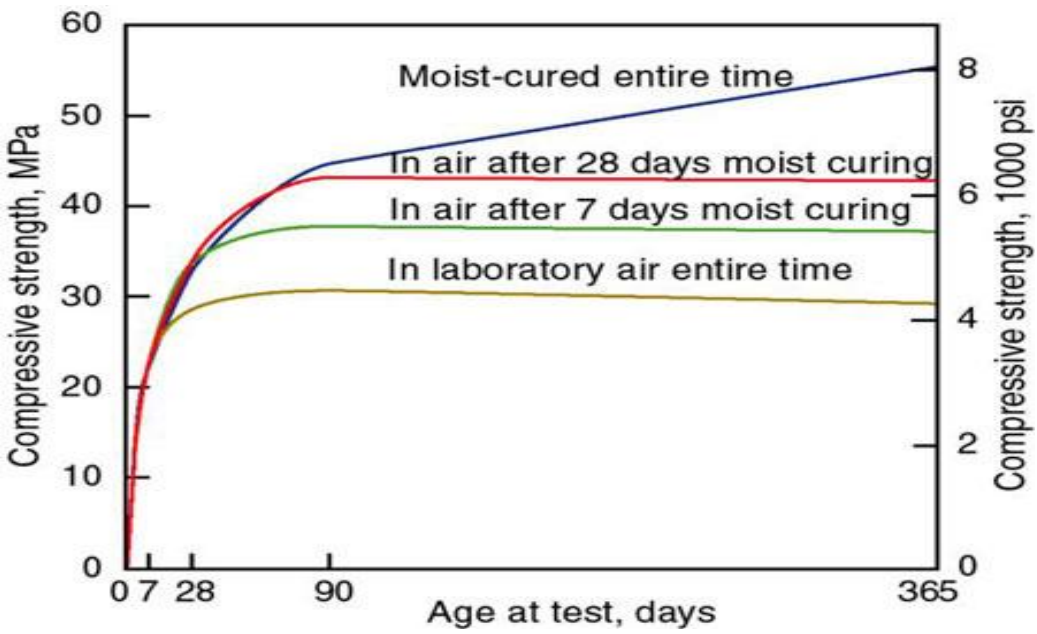

Figure 1-4: The change in strength with respect to the age of concrete

Mixing time is very important in increasing the strength of concrete. Researches shew that increasing the time of mxing results in increasing the compressive strength of concrete, generally specifications require 1 to 2 minutes mixing [7].

Curing in moisture or water is known as a very effctive factor in increasing the the strength of concrete. It is well assumed fact that curing concrete in moisture or water makes concrete gain more strength, because the water inside is prevente from evaporating. In cases when the concrete is cured in a dry environment, it was noticed that the strength decreases because of the less hydration due to the lack of water [7].

Temperature of curing has a significant affect on the strength. The concretes, that cured in cold environments, have less strength with respect to the concretes cured in warm environments [7].

Admixtures some meterials added to concrete during the mixing to improve its mechnical properties of concete. Admixtures are divided to two parts: chemical admixtures and mineral admixtures. In the next session more information, about admixtures and the purposes they are used for, will be given.

1.4 Admixtures

Admixture is a material added to the components of concrete either directly before mixing or during mixing. This definition is the same one which is mentioned in in the turkish standards (TS EN 934-2) [8].

1.4.1 Chemical Admixtures

Chemical admixtures are used for special purposes like, air entrainment, workability, color, cement dispersion, early strength and waterproof.

1.4.2 Mineral additives

Mineral additives make mixtures more economical, reduce permeability, increase strength, and influence other concrete properties. Mineral admixtures affect the nature of the hardened concrete through hydraulic or pozzolanic activity. Pozzolans are cementitious materials and include natural pozzolans (such as the volcanic ash used in Roman concrete), the widely used types of those mineral additives or admixtures are silica fume and fly ash.

1.4.2.1 Silica fume

Silica fume can significantly affect the early-age strength of concrete. Silica fume improves concrete in two ways the basic pozzolanic reaction, and a microfiller effect. Addition of silica fume improves bonding within the concrete and helps reduce permeability, it also combines with the calcium hydroxide produced in the hydration of portland cement to improve concrete durability [8].

As a microfiller, the extreme fineness of the silica fume allows it to fill the microscopic voids between cement particles.This greatly reduces permeability and improves the paste-to-aggregate bond of the resulting concrete compared to conventional concrete [8].

1.4.2.2 Fly ash

Fly ash is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Burning in the power pants, coal leaves molten particles rich in silica, alumina and calcium, after solidifying those particles are collected from the power plant. The collected material is very fine and easy to fly, therefore it is called fly ash [9].

Having special content of silica, alumina and calcium, fly ash considered to be a pozzolan. Pozzolan is a siliceous, or siliceous and aluminous, material which in itself possesses little or no cementitious value but will, in finely divided form and in the presenceof moisture, chemically react with calcium hydroxide at ordinary temperaturesto form compounds possessing cementitious properties – ASTM C125.

Accodring to the chemical content of fly ash, it is divided to two types. High calcium oxide content fly ash is called fly ash C class, so the low calcium oxide content fly ash is called fly ash F class.

CHEMICAL COMPOUND	POZZOLAN TYPE			CEMENT
	CLASS F	CLASS C	CLASS N	
SiO	54.90	39.90	58.20	22.60
Al_2O_3	25.80	16.70	18.40	4.30
Fe_2O_3	6.90	5.80	9.30	2.40
CaO	8.70	24.30	3.30	64.40
MgO	1.80	4.60	3.90	2.10
SO_3	0.60	3.30	1.10	2.30
Na_2O & K_2O	0.60	1.30	1.10	0.60

Figure 1-5: Typical chemical compounds in pozzolans and portland cement [9].

The reaction of fly ash in concrete is initiated after 1 or more weeks, in this period of time fly ash acts as precipitation factor for $Ca(OH)_2$ and C-S-H produced as a result of cement hydration [10].

The pozzolanic activity of fly ash depends on the reaction of SiO_2 and Al_2O_3 with $Ca(OH)_2$ to produce the gel of calcium silicate hydrate (C-S-H) [11].

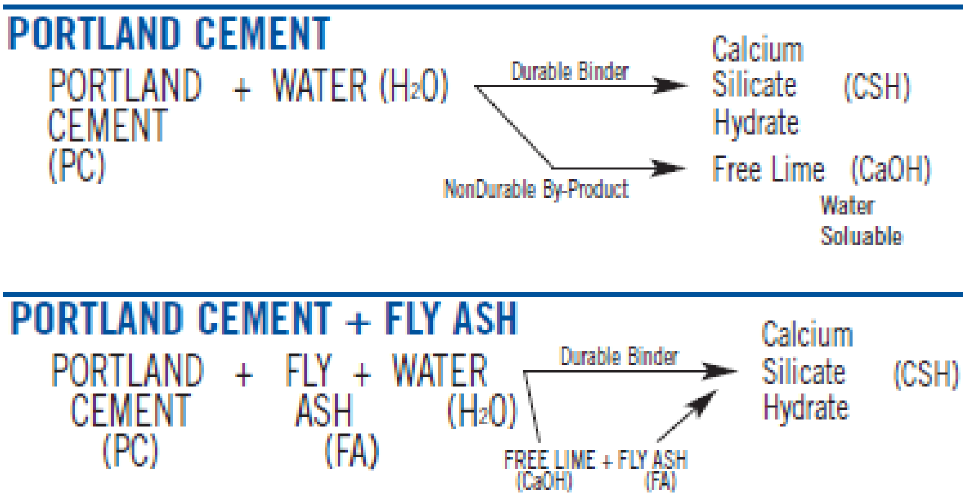

Figure 1-6: Hydration of cement in the presence of fly ash [9].

1.5 pH in concrete

Alkali (sodium hydroxide NaOH and potassium hydroxide KOH) is another natural component of concrete. New, wet concrete has a high alkalinity with a pH reading of 12-14 but typically drops with the carbonation of the concrete [11]. During the curing and drying of concrete or whenever moisture vapor is present, the moisture will dissolve the alkali salts. Hence, it is important to measure the pH of the concrete. However, there are two comman methods or measurement, the first one is by powder of concrete in distilled water solution and the second is measuring the extracted pore solution from the concrete.

1.5.1 Measurement of concrete pH by powder solution

This method is explained in [12], Rasanen et al. showed that some samples of concrete are crushed with grinding machine, then 30 gr of it was powdered for 20 s. Afteall, 15 gr of the powder is taken and mixed with 15 gr of the distilled water. The solution is mixed by a mixer machine for 15 min. after mixing the solution pH is measured by electronic pH meter [12].

1.5.2 Extraction of pore solution

The hydration process of cement can be considered as a sequence of chemical reactions between the solid compositions in cement and the mixing fluid [13]. Therefore, it is important to examine the solution entrapped on the voids which called pore solution.

Barneyback et al. [13], was one of the first ppl who invastigated the ways and the methods to exrtact the pore solution to apply the different measurements.

To extract the pore solution, high compression force is applied to squeeze the concrete fragments and to carry out such an operation. Barneyback states that the apparatus applies a pressure about 550 MPa to about 250 g of cement paste for siutable period of some minutes to be able to exrtact enough amount of pore solution [13].

Pore solution expression from concrete has been a very famous method to get the entrapped water in the voids of the cement paste to carry about needed chemical tests on it [14].

A modern designed device was shown by Cyr et al. [15]. The device has the capacity to apply up to 1000 MPa on the specimen, shown in the figure below.

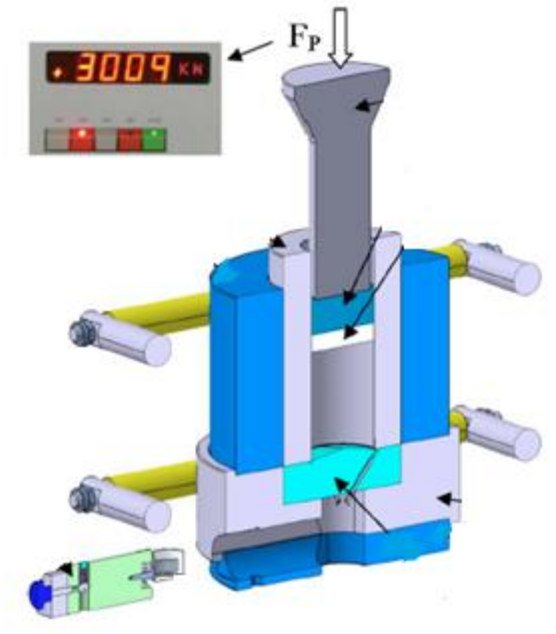

Figure 1-7: Pore solution extraction device [15]

As it is seen in Figure 1-7, the device consists of several parts but it can be summarized in four main parts, the first part is a base that holds all the pieces, the second part is two cylinders (outer cyliner and inner cylinder), piston to transfer the load from the compression machine to the inner cylinder to squeeze the fragment inside.

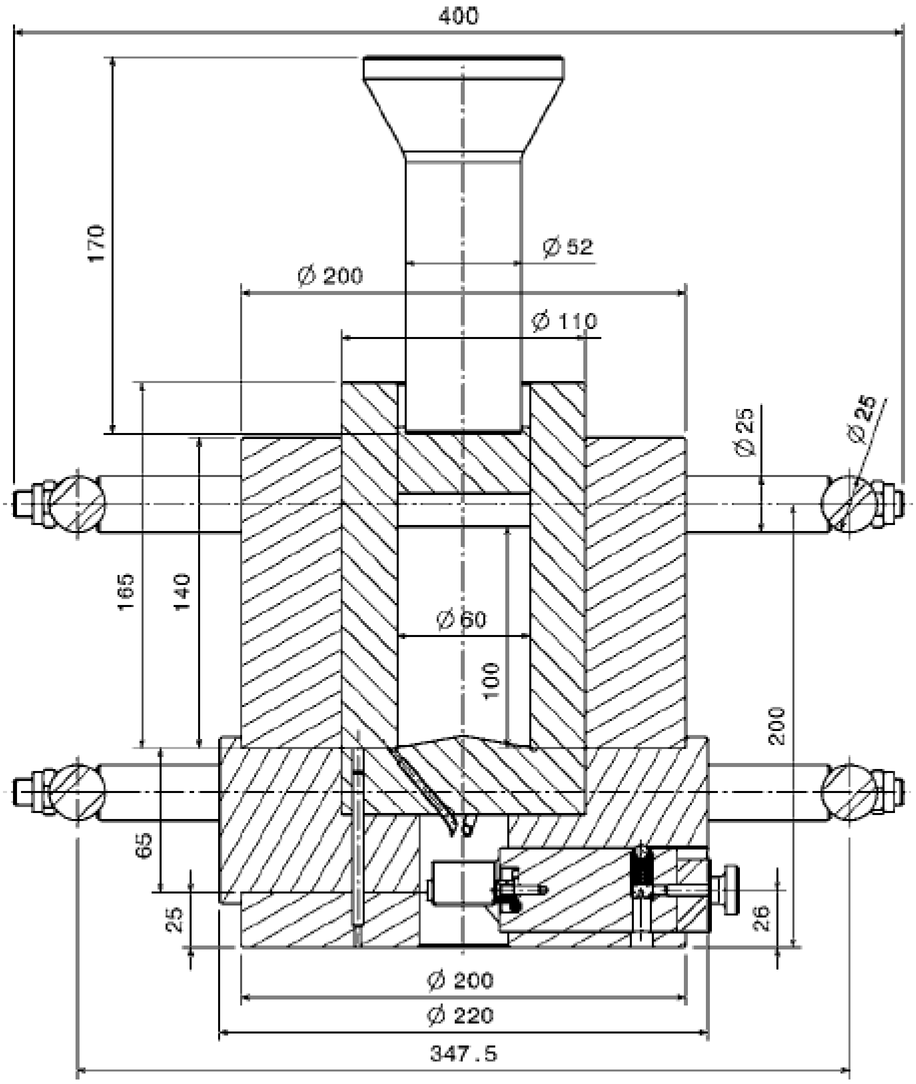

Figure 1-8: Schematic diagram of high-pressure one-dimensional device [15]

2. EXPERIMENTAL WORKS

2.1 Materials

2.1.1 Portland cement

The cement used in this research is AKÇANSA partland cement CEM I 42.5R. Its properties were designed according to TS EN 197-1 R Chemical properties are shown in the table below

Table 2-1: Chemical compositions (%) of cement

Component	Percentage
SiO_2	20,63
Al_2O_3	4,71
Fe_2O_3	3,41
CaO	63,64
MgO	1,24
SO_3	2,98
Na_2O	0,23
K_2O	0,91
Cl	0,91
Loss on ignition (%)	1,25
Free lime (%)	1,1
Specific Gravity(gr/cm3)	3.12

2.1.2 Fly ash

Two types o flyash were used. The first type was, taken from Çatalağzı thermic central, flyash with low lime (CaO) content known as F class. The second type was taken from Çayırhan thermic central as flyash with high lime (CaO) content, know as C class.

Table 2-2: Chemical composition and physical properties of fly ashes

Component (%)	Flyash (F)	Flyash (C)
H_2O	0,2	0,2
SiO_2	58,5	46,38
Al_2O_3	23,4	13,9
Fe_2O_3	6,97	8,26
CaO	1,55	15,1
MgO	2,76	6,68
SO_3	0,45	4,26
Na_2O	0,46	2,13
K_2O	4,11	2,78
Cl	0,0319	0,0638
Loss on ignition (%)	0,2	0,22
Free lime (%)	0,15	0,15
Specific Gravity(gr/cm3)	1,84	2,3

2.1.3 Aggregates

Two sizes of crushed stones (limestone) as coarse aggregates, and one crushed stone sand (limestone) and natural sand as fine aggregates were used. The grading and specific gravities of the aggregates are shown in Tables 2-3 and 2-4.

Table 2-3: Aggregate grading (Passing %)

Sieve size (mm)	32	16	8	4	2	1	0,5	0,25
Crushed stone II	100	55.6	5.9	4.5	3.4	2.9	0	0
Crushed stone I	100	100	78	26.8	11.9	7.3	5.8	4.4
Crushed sand	100	100	99.2	77.9	47.5	35.9	20.2	9.6
Natural sand	100	100	100	100	99	98.3	97.3	4.1
Agg. mixture grading	100	85.8	63.7	44.1	32	27.6	22.2	4.2

Table 2-4: Specific weights of the aggregates

Material	Specific weight (gr/cm^3)
Crushed stone II	2.73
Crushed stone I	2.73
Crushed sand	2.71
Natural sand	2.68

2.1.4 Chemical admixture

The plasticizer used in the experiment is superplasticizer Glenium 51 (water reducer). İt was used as 1% of the cement weight in the mixture and only used in mixtures with low water-to-binder ratio (0.45, 0.50, 0.55).

2.2 Production of concrete

In this concrete mixture, a constant proportions of aggregates, were used. The proportions were as: 16 % natural sand, 25 % crushed sand, 27 % crushed stone I and 32 % crushed stone II. The grading ratios of the aggregate mixture are given in Table 3-3, and also shown in Figure 2-1 together with the reference curves of TS 706. All the concretes were produced according to those proportions for all the water to binder ratios.

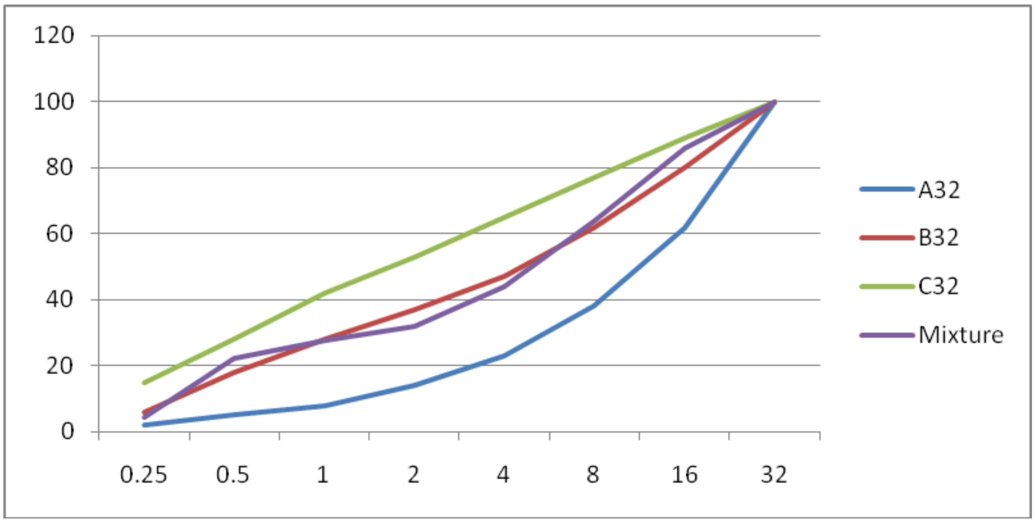

Figure 2-1: Grading curve of aggregate mixture and reference curves

Constant binder (cement+fly ash) dosage was used as 325 kg/m^3 and six different water-to-binder ratios were used in production of concrete as follows: 0.45, 0.50, 0.55, 0.60, 0.65, 0.70. Fly ash added concretes with both types, F class and C class, and reference concretes without fly ash were produced. Fly ash was used as 20% replacement of cement weight in all fly ash added concretes for both types, F class and C class. For keeping the concretes in a certain level of workability, a contant slump was taken for all the produced mixtures (15~17cm) and a superplasticizer was used in low w/binder concretes.

In the table below, the proportions of each concrete group, were shown.

Table 2-5: Components of concrete mixture

specimen	cement (kg/m^3)	Flyash (kg/m^3)	sand (kg/m^3)	C.sand (kg/m^3)	C.stone I (kg/m^3)	C.stone II (kg/m^3)	water (kg/m^3)
PC45	325	0	315	492	541	641	146
PC50	325	0	308	481	529	627	163
PC55	325	0	301	470	517	613	179
PC60	325	0	294	459	505	599	195
PC65	325	0	287	448	493	584	211
PC70	325	0	280	437	481	570	228
FF45	260	65	308	481	529	627	146
FF50	260	65	301	470	517	613	163
FF55	260	65	294	459	505	599	179
FF60	260	65	287	449	493	585	195
FF65	260	65	280	438	481	571	211
FF70	260	65	273	427	469	556	228
CF45	260	65	313	489	538	638	146
CF 50	260	65	306	478	526	623	163
CF55	260	65	299	467	514	609	179
CF60	260	65	292	456	502	595	195
CF65	260	65	285	445	490	581	211
CF70	260	65	278	435	478	567	228

PC: Plain Concrete, FF: F class Flyash added concrete, CF: C class Flyash added concrete

After proportioning the ingredients, they were mixed in a mixer with a capacity of 40 dm^3 for at least 2 min. High range water reducer was added during mixing for low water-to-binder ratios (0.45, 0.50 and 0.55). At the end of mixing, the slump of concrete was tested to insure the limit of 15-17cm slump for all the mixtures. Then, fresh concrete was poured into plastic cubes (15x15x15) cm, they were vibrated immediately after pouring to insure the compaction of the mixture inside the cubic frame.

The specimens were kept in water at a temperature between 21-23 ^{o}C and divided for three ages with three specimens for each age (7 days, 28 days and 90 days) of the eighteen groups produced.

2.3. Tests

2.3.1 Compressive strength

At the end of every certain age, specimens were prepared and tested for compressive strength according to TS EN 12390-3 by the compressive testing machine of ELE AUTOTEST3000 with capacity of 3000 kN (Figure 3-2).

Figure 2-2: Compressive strength testing machine (ELE AUTOTEST3000)

2.3.2 pH measurement

Two methods were applied to get the pH, the first one was measuring the pH of the suspended solution of the concrete powder, which is pulvurized from the specimen, the second method was extraction of pore solution.

As soon as a compressive strength test finished, a part of the tested specimen was taken and pulverized to apply the measurement of pH.

2.3.2.1 Suspended solution

In this method, the inner part of the specimen is pulverized to very fine powder, so it passes from sieve size 0.25 mm. The samples are pulverized very finely to get the best result for pH. 15 g from the finely crushed sample is taken and mixed with 15 g of distilled water then the mixture was put in the mixer of GALLENKAMP (Figure 2-3) for 20 minutes to insure the homogeneity.

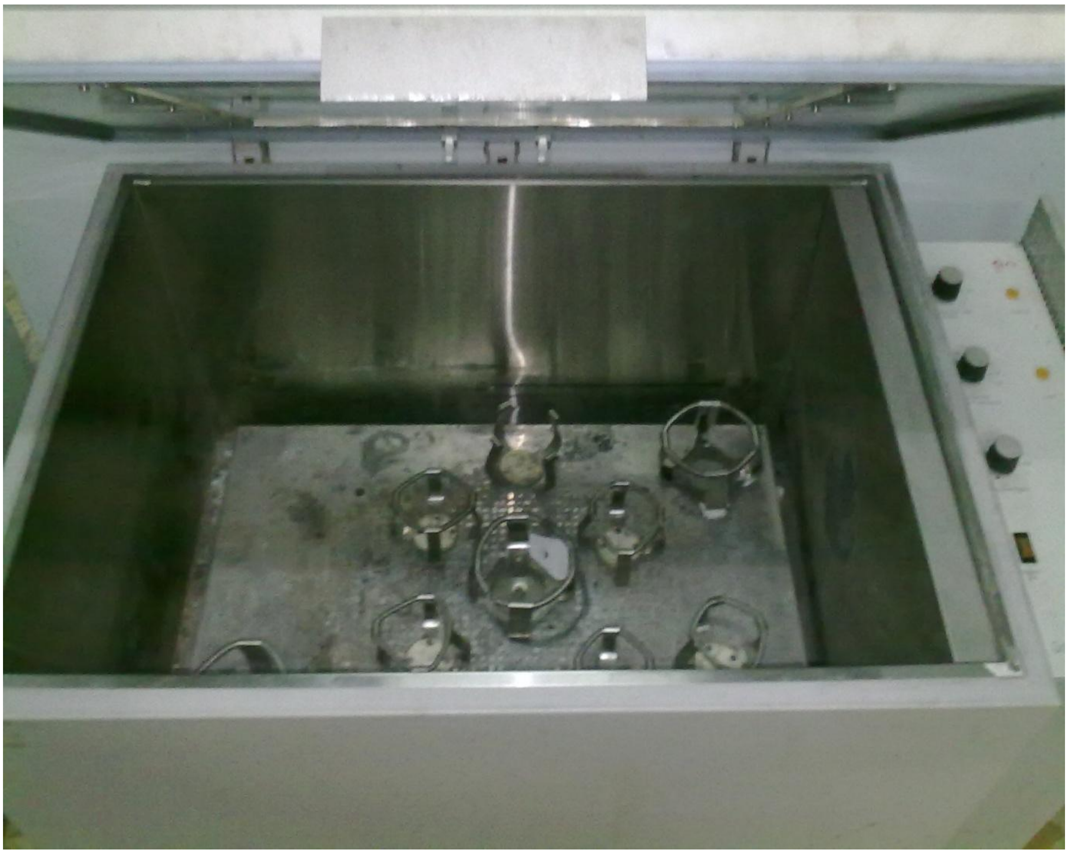

Figure 2-3: Mixer of GALLENKAMP

As soon as the mixture is taken from the mixer after 20 minutes, the pH is measured by the digital pH meter, which is Thermo Orion 500A+ with accuracy of 0.002 pH.

Figure 2-4: Thermo Orion 500A+ pH meter

2.3.2.2 Extraction of pore solution

The deviced used in this research is shown in the Figure 2-5, which is almost similar to the one used by Cyr et al. [13] with some modifications. The device consists four main parts, the first part is a base that holds all the pieces, the second part is two cylinders (outer cyliner and inner cylinder), piston to transfer the load from the compression machine to the inner cylinder to squeeze the fragment inside.

The tested specimen is crushed into small parts about (1-2) cm size, then about 250 g of the inner part was taken to be used in pore solution extraction device. Concrete samples were put in the inner cylinder of the device covered by a disk of hard teflon to prevent the lose of pressure and to keep the water inside. The pressure is applied on the specimen by a compression machine (Figure 3-6) with capacity of 250 t, and the load was transfered to the specimen by a piston.

The load was applied for 15 minutes until it reached about 560 MPa at the 0.6 MPa/s constant rate of loading. At the end of the squeezing processing, the load was released and the extracted water was taken and stored in sealed glass tube to prevent the carbonation of the pore solution.

The pH of the extracted pore solution was measured in the laboratory by the same pH meter (Thermo Orion 500A+) mentioned above.

Figure 2-5: Pore solution exraction device

Figure 2-6: Pore solution extraction device connected to compression machine

3. TESTING RESULTS

3.1 Compressive strength results

Compressive strength results of the concrete without fly ash are given in Table 3-1. The variation of the compressive strength with respect to water-to-binder ratio for different ages is shown in Figure 3-1.

Table 3-1: Compressive strength of plain concrete

Concrete without fly ash	Compressive strength (MPa)		
w/b	7 days	28 days	90 days
0.45	52.86	53.49	55.38
0.50	50.53	51.47	54.28
0.55	34.99	37.72	46.05
0.60	33.18	36.95	38.53
0.65	28.51	32.44	36.85
0.70	25.24	29.69	30.37

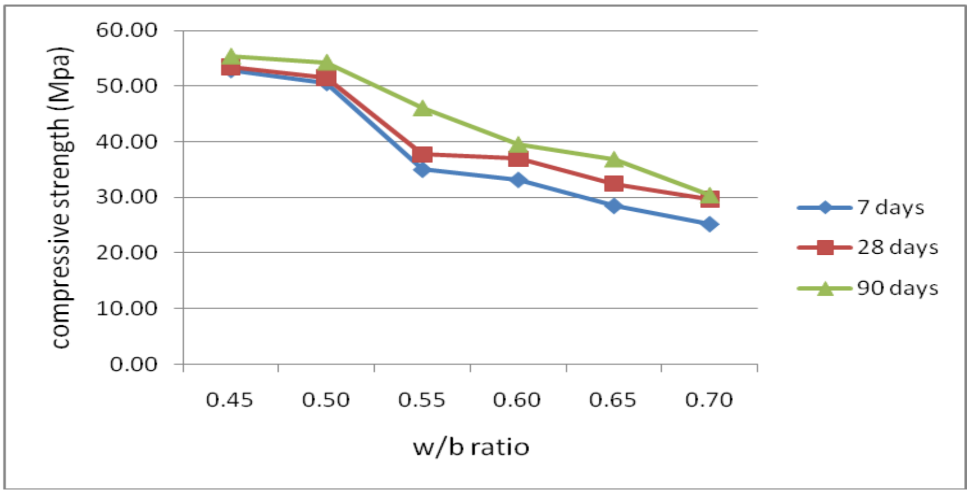

Figure 3-1: The variation of compressive strength for concretes without fly ash with water-to-binder ratio at different ages

The change of the compressive strength of F class fly ash added concretes with different water-to-binder ratios at different ages is given in Table 3-2 and Figure 3-2.

Table 3-2: Compressive strengths of F class fly ash added concretes

F Class Flyash concrete		stress	
w/b	7 days	28 days	90 days
0.45	38.85	42.29	53.11
0.50	31.87	39.71	47.87
0.55	29.91	36.33	46.90
0.60	26.38	34.27	41.91
0.65	23.65	25.66	36.85
0.70	18.19	22.70	32.20

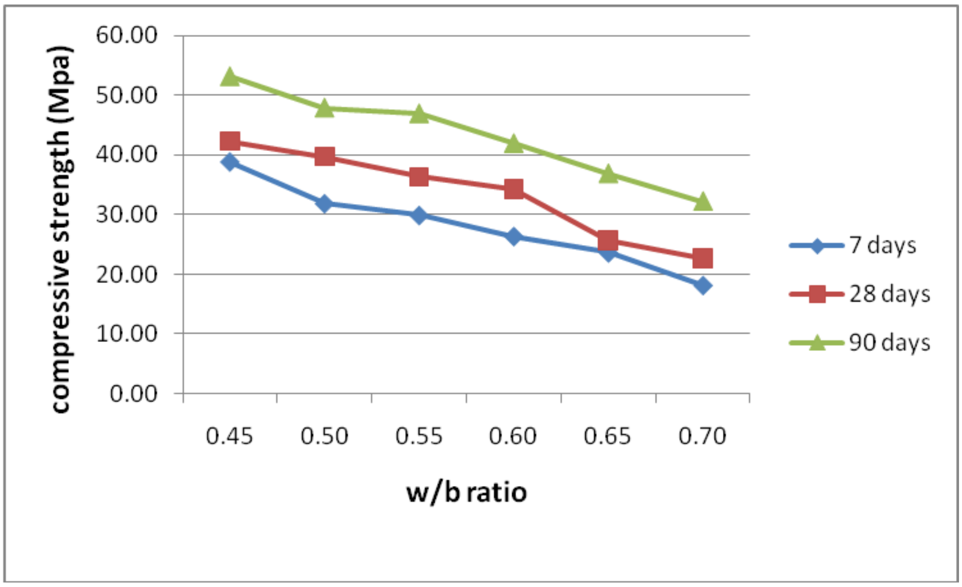

Figure 3-2: The variation of compressive strength for F class fly ash added concretes with water-to-binder ratio at different ages

Table 3-3 and Figure 3-3 show the change of the compressive strength of C class fly ash-added concretes with different water-to-binder ratios at different ages is given in.

Table 3-3: Compressive strengths of C class fly ash-added concretes

C Class Flyash concrete		stress	
w/b	7 days	28 days	90 days
0.45	40.70	41.24	47.27
0.50	37.15	41.23	45.37
0.55	33.00	39.17	44.80
0.60	27.17	31.95	44.38
0.65	22.10	27.26	34.78
0.70	18.04	22.56	30.84

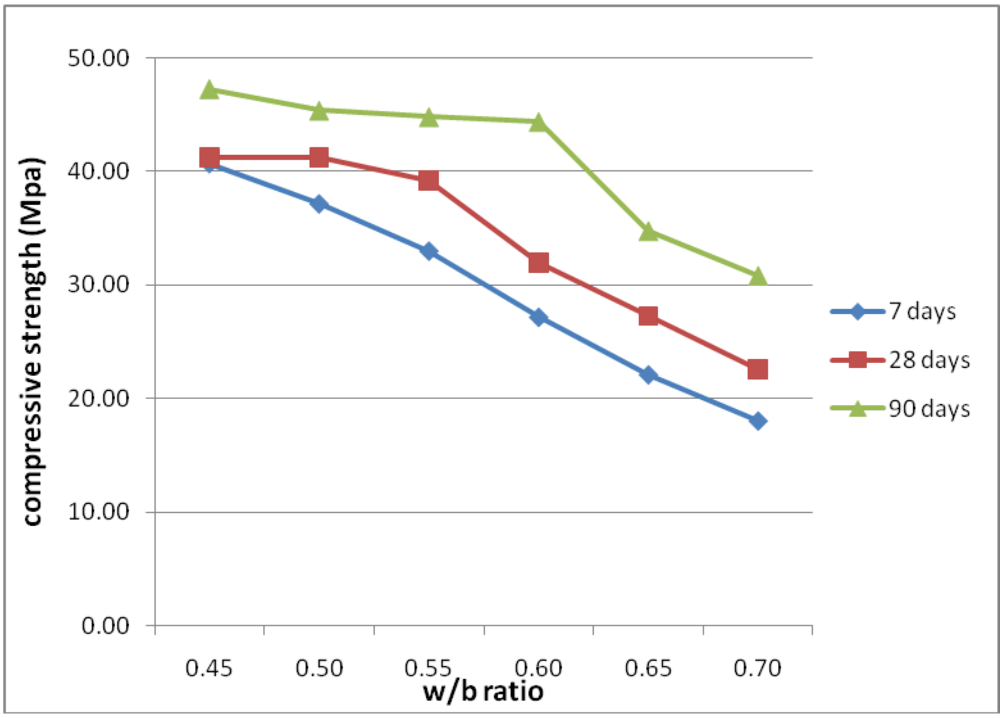

Figure 3-3: The variation of compressive strength for C class fly ash added concretes with water-to-binder ratio at different ages

3.2 pH measurement results

Initially pH tests were made by pore solution extraction method, but it was found that for w/b ratio smaller than 0.60 and at later ages (90 days) the amount of extracted water was not enough to carry out pH measurement. For this reason, at later tests, both pore solution extraction and powder solution methods were applied and a conversion ratio was calculated to obtain pH measured by the latter method by using the former method test results.

The pH measurement results made by powder solution and pore solution extraction methods are shown in Tables 3.4-3.6.

Table 3-4: Comparison between pH values of F type fly ash added concretes measured by powder solution method and pore solution extraction method

Age (day)	w/b ratio	Powder Solution (PWS)	Pore Solution (PS)	PS/PWS
7	**0.60**		13.60	
	0.65		13.68	
	0.70		13.45	
28	**0.60**	13.05	13.64	1.05
	0.65	13.14	13.58	1.03
	0.70	13.10	13.60	1.04

Table 3-5: Comparison between pH values of C type fly ash added concretes measured by powder solution method and pore solution extraction method

Age (day)	w/b ratio	Powder Solution (PWS)	Pore Solution (PS)	PS/PWS
7	**0.60**		13.68	
	0.65		13.73	
	0.70		13.51	
28	**0.60**	13.09	13.68	1.05
	0.65	13.25	13.68	1.03
	0.70	13.15	13.63	1.04

Table 3-6: Comparison between pH values of plain concretes measured by powder solution method and pore solution extraction method

Age (day)	w/b ratio	Powder Solution (PWS)	Pore Solution (PS)	PS/PWS
7	**0.60**		13.70	
	0.65		13.73	
	0.70		13.70	
28	**0.60**	13.10	13.71	1.05
	0.65	13.18	13.73	1.04
	0.70	13.17	13.65	1.04

The ratios of PS/PWS given in Tables 3.4-3.6 show the ratios of pH results obtained by pore solution extraction and powder solution methods, respectively. The average value of these ratios is calculated as conversion coefficient.

Conversion Coefficient=(1.05+1.03+1.04+1.05+1.03+1.04+1.05+1.04+1.04)/9=1.04

By using the conversion coefficient of 1.04, the values of pH obtained by pore solution extraction method were converted into those of powder solution method, as shown in Tables 3.7-3.9.

The pH values obtained on concretes without fly ash are given in Table 3-7 and Figure 3-4.

Table 3-7: pH values of concretes without fly ash

Plain Concrete		pH	
w/c	7 days	28 days	90 days
0.45	13.15	13.14	12.73
0.50	13.21	13.26	12.86
0.55	13.15	13.27	12.89
0.60	13.18*	13.10	12.85
0.65	13.21*	13.18	12.82
0.70	13.18*	13.17	12.91

*Calculated from pore solution extraction pH results by using conversion coefficient.

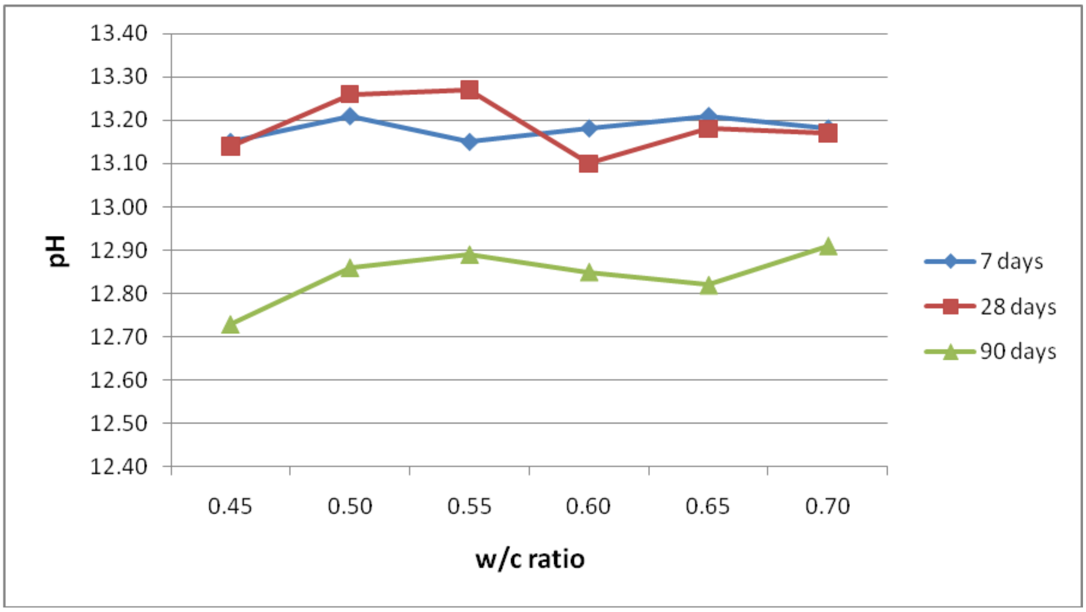

Figure 3-4: Relation between pH of plain concrete at different ages

The pH values measured on concretes prepared with F class fly ash are given in Table 3-8 and Figure 3-5.

Table 3-8: pH values of F class fly ash added concrete

F class fly ash added Concrete		pH	
w/c	7 days	28 days	90 days
0.45	13.10	13.18	12.77
0.50	13.13	13.23	12.82
0.55	13.08	13.18	12.92
0.60	13.09*	13.05	12.95
0.65	13.16*	13.14	12.91
0.70	12.94*	13.10	12.85

*Calculated from pore solution extraction pH results by using conversion coefficient.

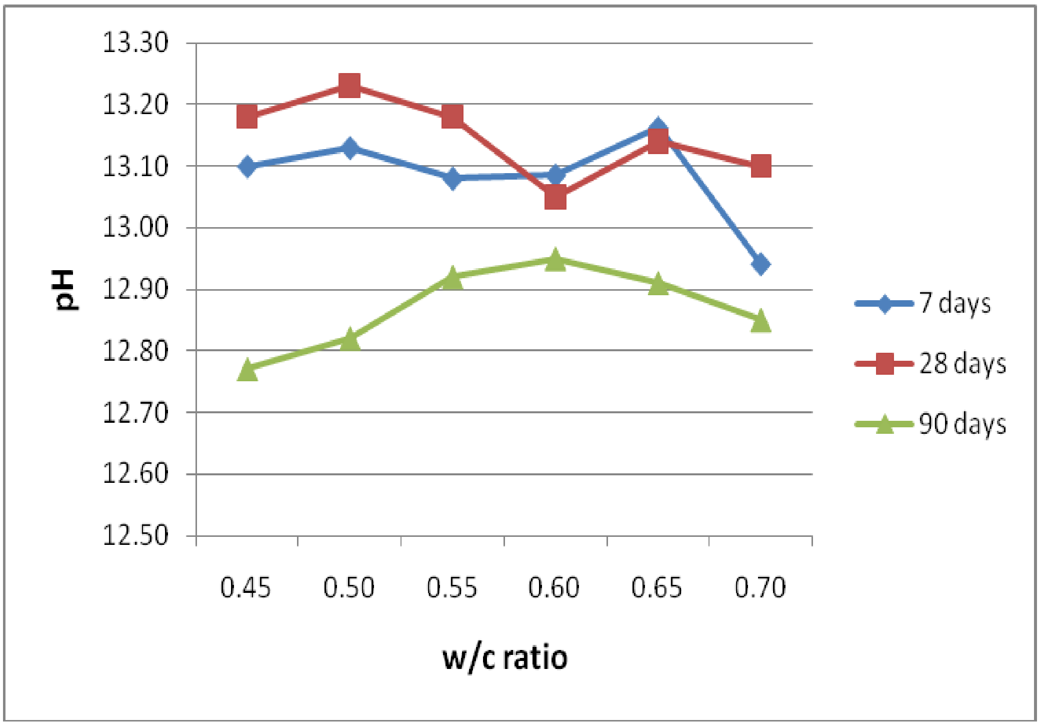

Figure 3-5: Relation between pH of F class fly ash added concrete at different ages

For C class fly ash added concretes, the pH values for different w/b ratios at different ages are shown in Table 3-9 and figure 3-6.

Table 3-9: pH values of C class fly ash added concrete

C class fly ash added Concrete		pH	
w/c	7 days	28 days	90 days
0.45	13.10	13.09	12.83
0.50	13.18	13.25	12.91
0.55	13.08	13.15	12.93
0.60	13.16*	13.09	12.96
0.65	13.21*	13.25	12.91
0.70	13.00*	13.15	12.91

*Calculated from pore solution extraction pH results by using conversion coefficient.

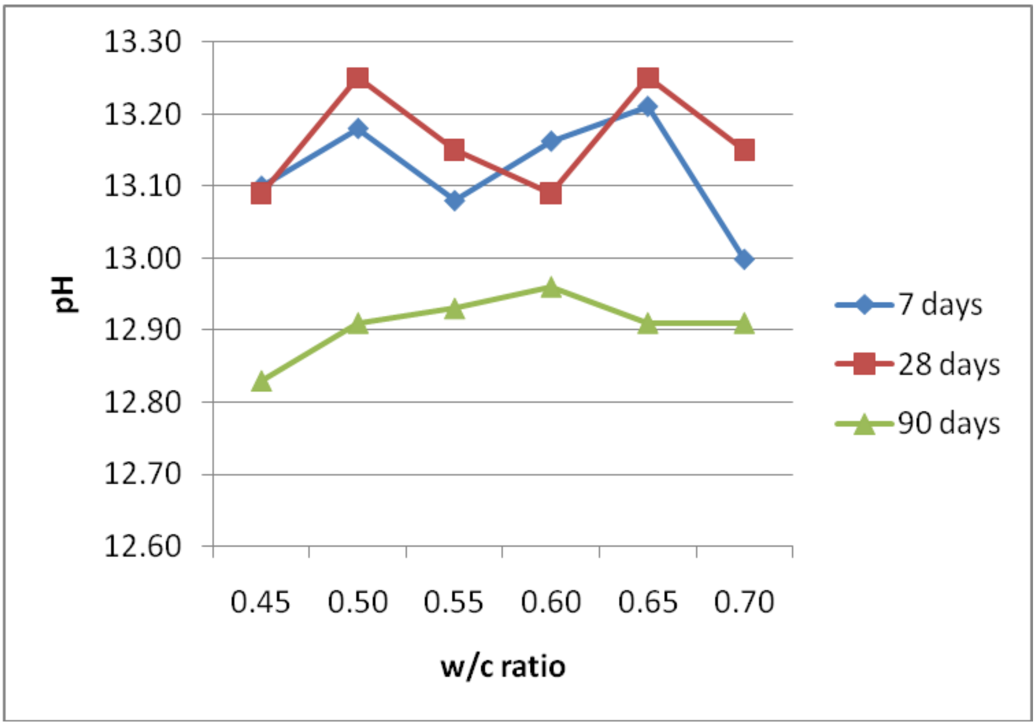

Figure 3-6: Relation between pH of C class fly ash added concrete at different ages

4. DISCUSSION of TEST RESULTS

4.1 Compressive strengths

7-day strength results are shown in Figure 4-1. In this figure it is clear that the plain concrete has higher compressive strength than the fly ash added concretes but it is obvious that at water to binder raio of 0.55 the three curves reach to a very close values and this can be the optimum value to be considered.

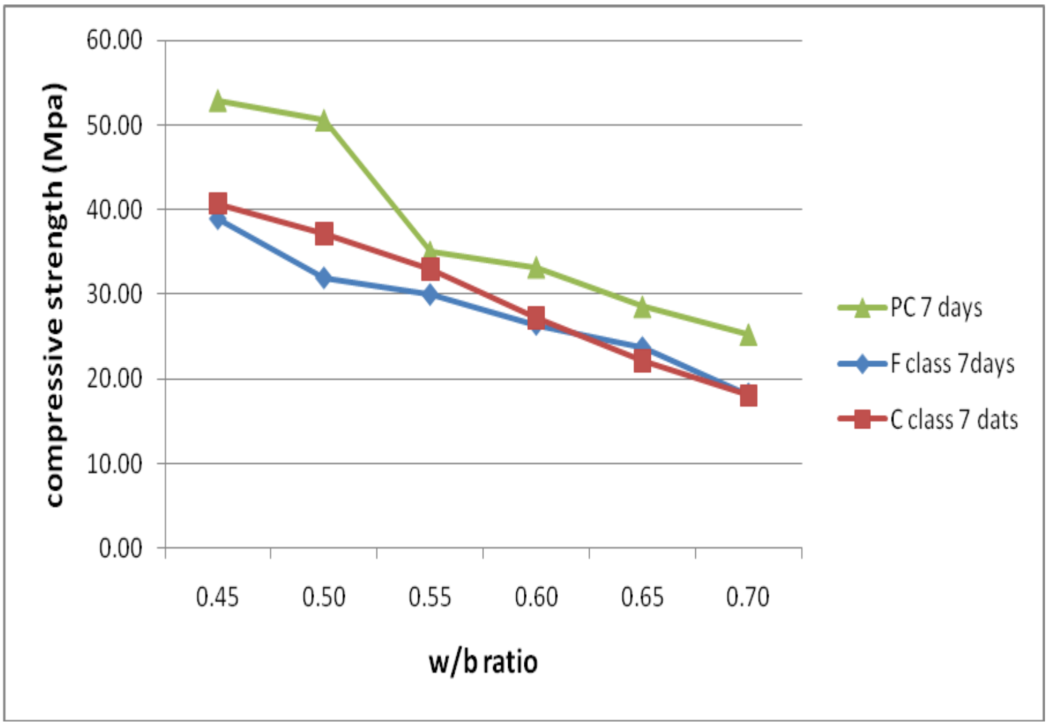

Figure 4-1: Relation between 7 days compressive strength of different concrete types with respect to water-to-binder ratio

In Figure 4-2, 28-day compressive strength results were given. The behavior seems to be similar to the one seen in Figure 4-1, i. e., plain concretes have the highest strengths, and the w/b ratio of 0.55 again appears to be an optimum point where the three types of concrete get very close values of compressive strength.

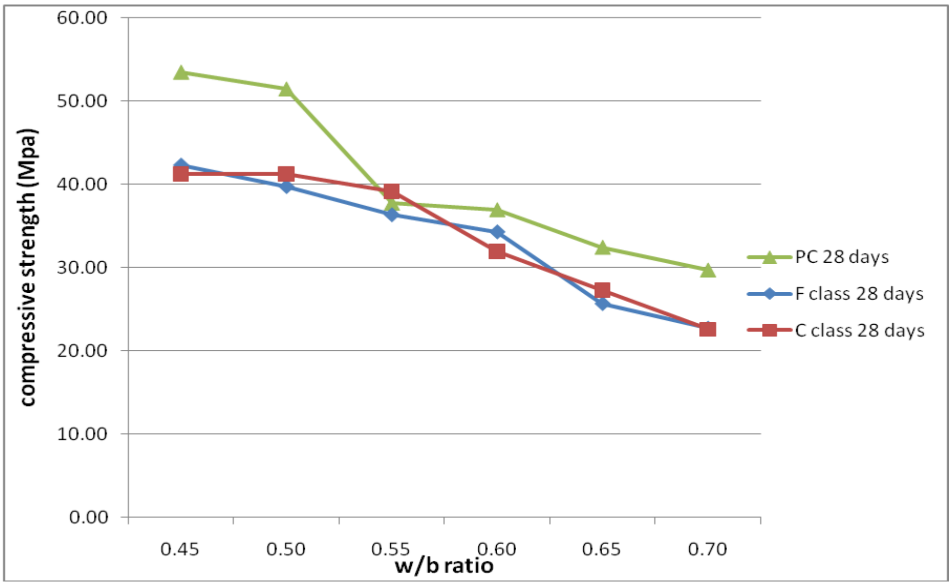

Figure 4-2: Relation between 28 days compressive strength of different concrete types with respect to water to binder ratio

90-day compressive strength results were given in Figure 4-3. In this case, the strengths of plain concretes are the highest for only w/b ratios of 0.45 and 0.50, but over them the fly ash added concrete strengths exceed the formers. Again 0.55 appears to be an optimum w/b ratio where the three types of concretes get very close to each other.

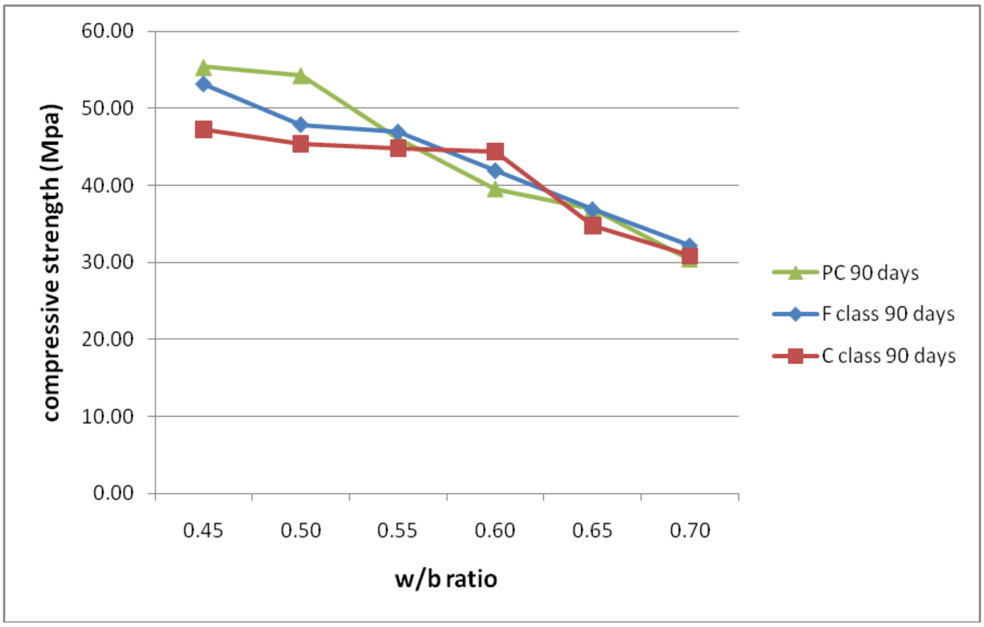

Figure 4-3: Relation between 90 days compressive strength of different concrete types with respect to water to binder ratio

4.2 Relative compressive strength

To see the change of the compressive strength of fly ash added concretes with respect to plain concrete, relative compressive strength is calculated. For a specific age, the strengths of the mixtures with fly ash (either F or C type) were divided by the corresponding strengths of the concretes, which are fly ash free, for the same w/c ratios; so relative strengths were obtained. The relative strengths of the concretes at the ages of 7, 28 and 90 days are shown in Figures 4-4, 4-5 and 4-6, respectively.

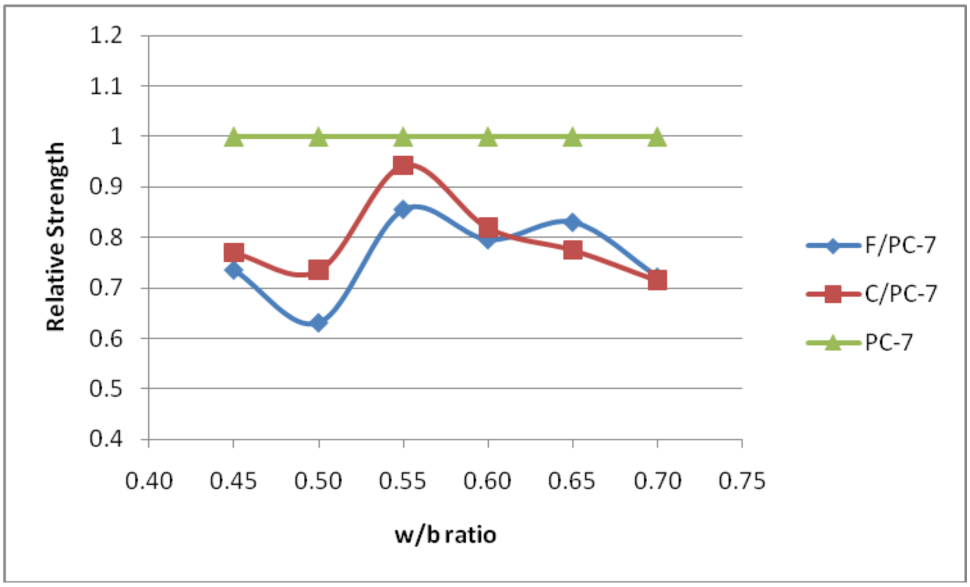

Figure 4-4: Relative strength of F class and C class fly ash added concretes in 7 days

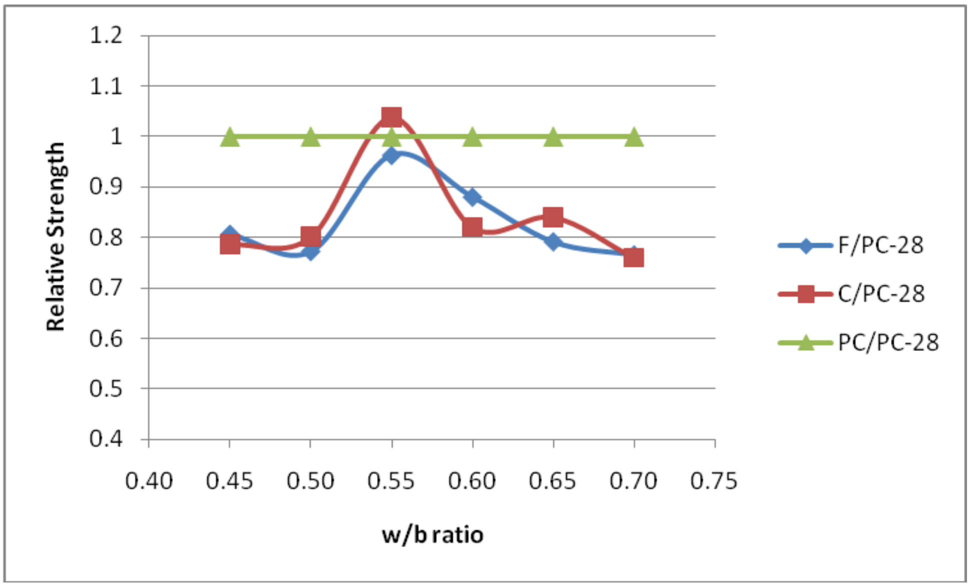

Figure 4-5: Relative strength of F and C class fly ash added concretes in 28 days

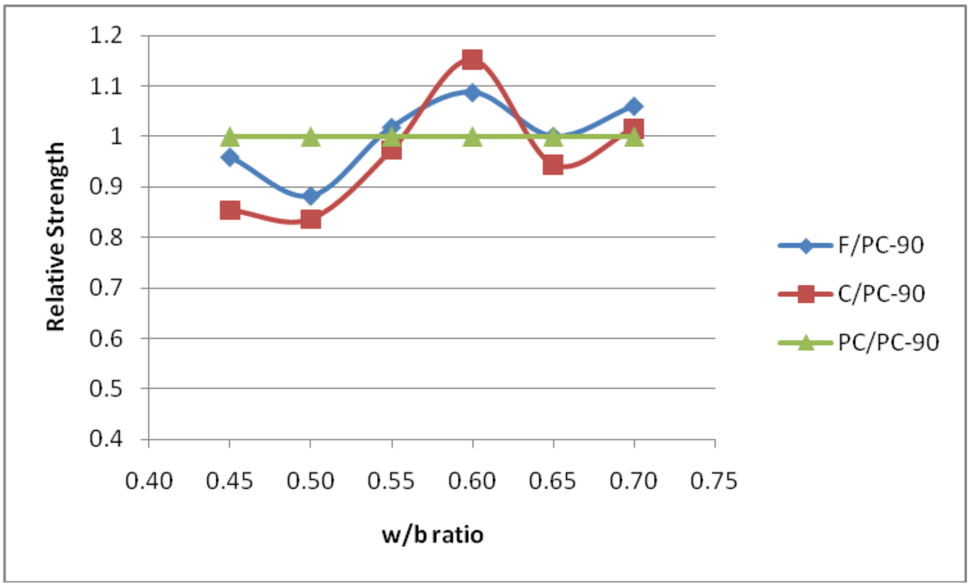

Figure 4-6: Relative strength of F class and C class fly ash added concretes in 90 days

At 7 and 28 days, the relative strengths of fly ash added concretes remained lower than the corresponding values of the plain concretes for all water-to-binder ratio (except one value of C class fly ash concrete at 28 days). On the other hand, the relative strengths fly ash added concretes were the highest at the w/b ratio of 0.55, which was defined as an optimum value in the previous section. Furthermore, at the age of 28 days these maximum values approached to that of plain concrete. At the age of 90 days, the strengths of all type of concretes reached almost the same level at the w/b ratio of 0.55, and immediately afterwards fly ash added concretes started to get higher strengths than the corresponding values of plain concrete.

4.3 pH measurement results

The results measured by pore solution extraction method could not be obtained for low w/b ratios (lower than 0.60) for all ages, morever, for 90 days no pore solution could be extracted. Therefore, the results obtained from powder solution method were used in the evaluation of the results. However, when the results of pH from both methods were compared with eachother (dividing the pH results from pore solution extraction method to the results from powder solution method), for each w/b ratio, approximately a constant number is obtain (1.04).

In Figure 5-7 it is obvious that the pH value of plain concrete at the age of 7 days is higher than the pH value of fly ash added concretes at the same age. The presence of fly ash in concrete decreases the cement content and this makes the hydration lower in the early ages [16] for fly ash added concretes..

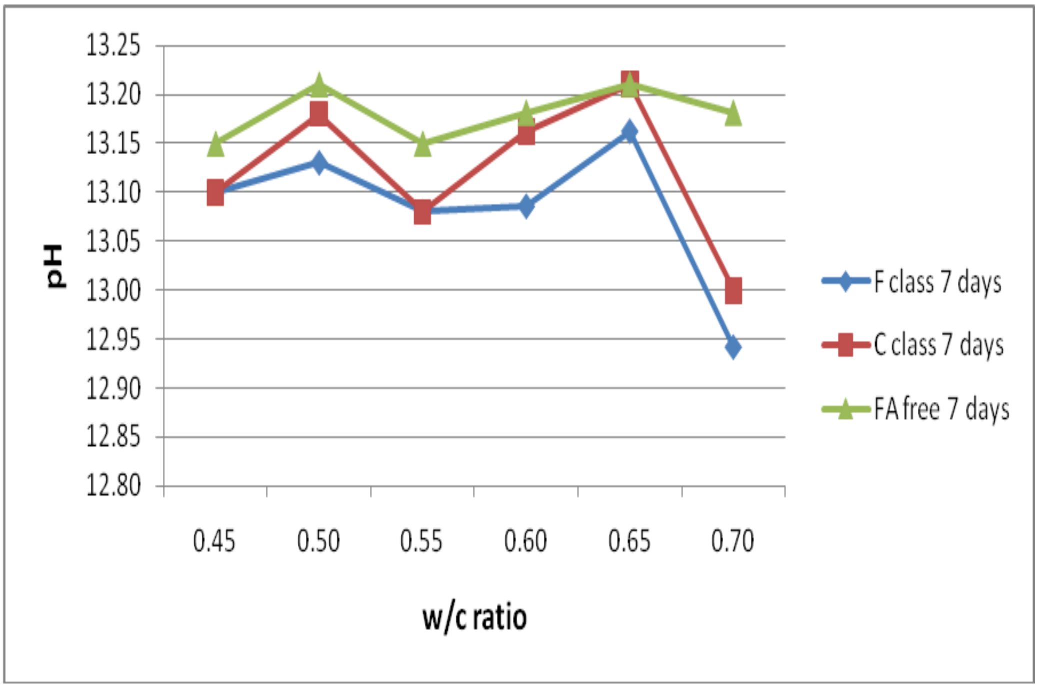

Figure 4-7: Relation btween pH values of 7 days age concretes

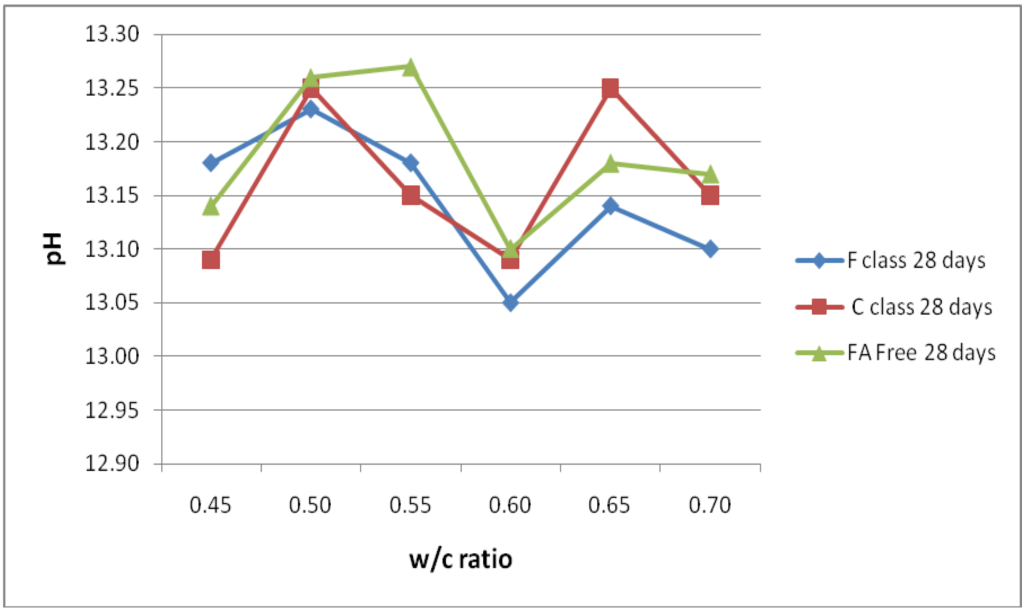

Figure 4-8: Relation between pH values of 28 days age concretes

Relation between pH values of 28 days age concretes given in Figure 4-8. This figure shows that the pH values of fly ash added concretes are lower than those of plain concretes due to the pozzolanic reaction, which consumes lime.

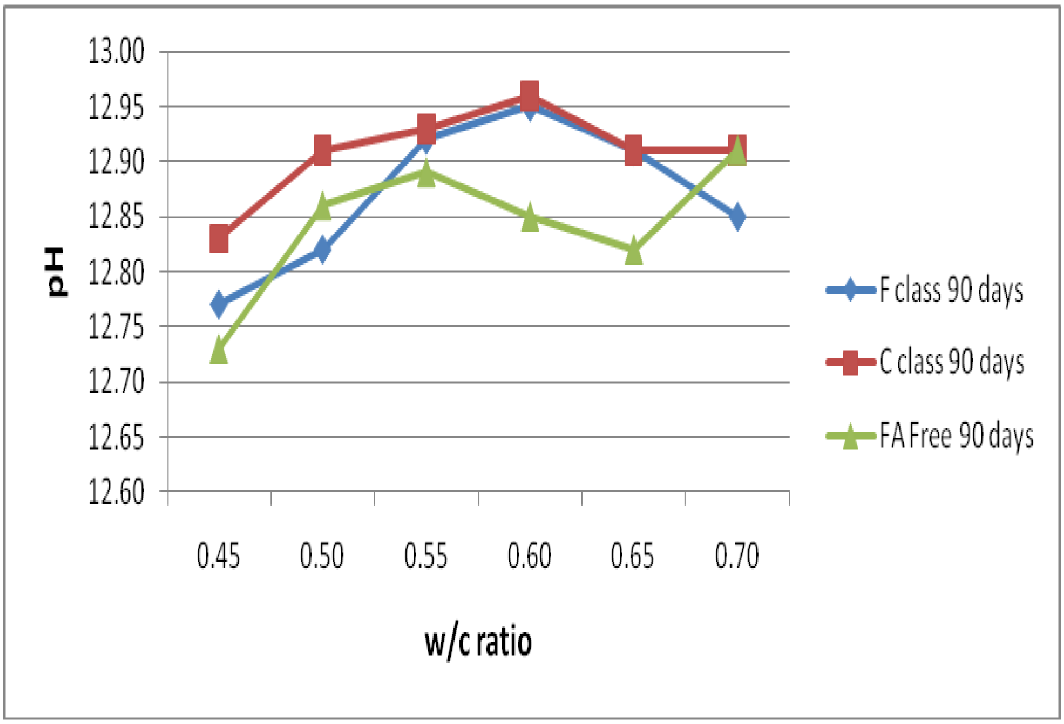

Figure 4-9: Relation btween pH values of 90 days age concretes

İn figure 4-9, the value of pH in fly ash free concrete decreased but at the same time it increased in fly ash added concretes and this can be due to the activity of fly ash in the pozzolanic reaction after 28 days [17].

4.4 Relative pH values

The change of the value of pH of fly ash added concretes with respect to plain concrete, can be seen clearer by calculating the relative pH. For a specific age, the pH of the mixtures with fly ash (either F or C type) were divided by the corresponding pH values of the concretes, which are fly ash free, for the same w/c ratios; so relative pH values were obtained. The relative pH values of the concretes at the ages of 7, 28 and 90 days are shown in Figures 4-10, 4-11 and 4-12, respectively.

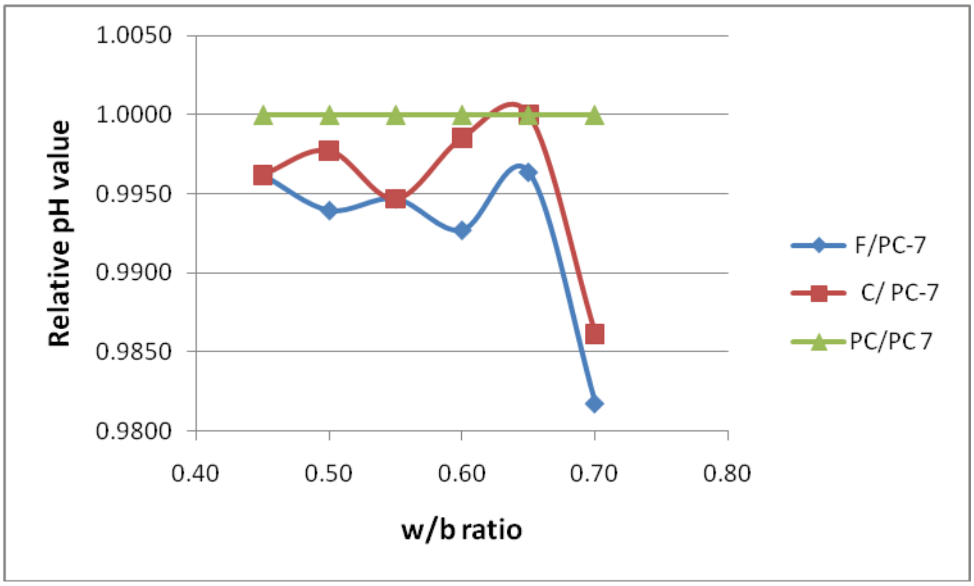

Figure 4-10: Relative pH value of concretes at 7 days

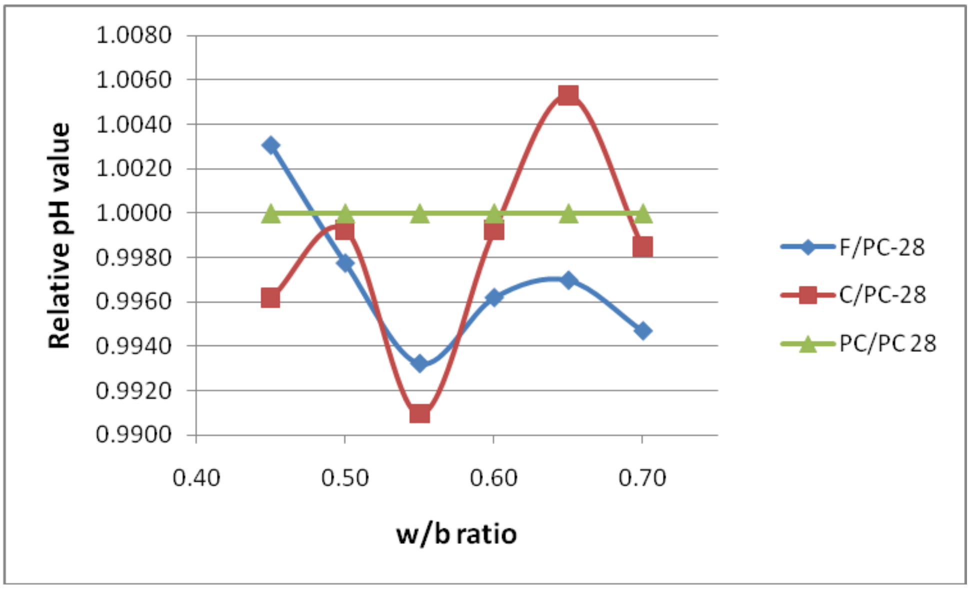

Figure 4-11: Relative pH value of concretes at 28 days

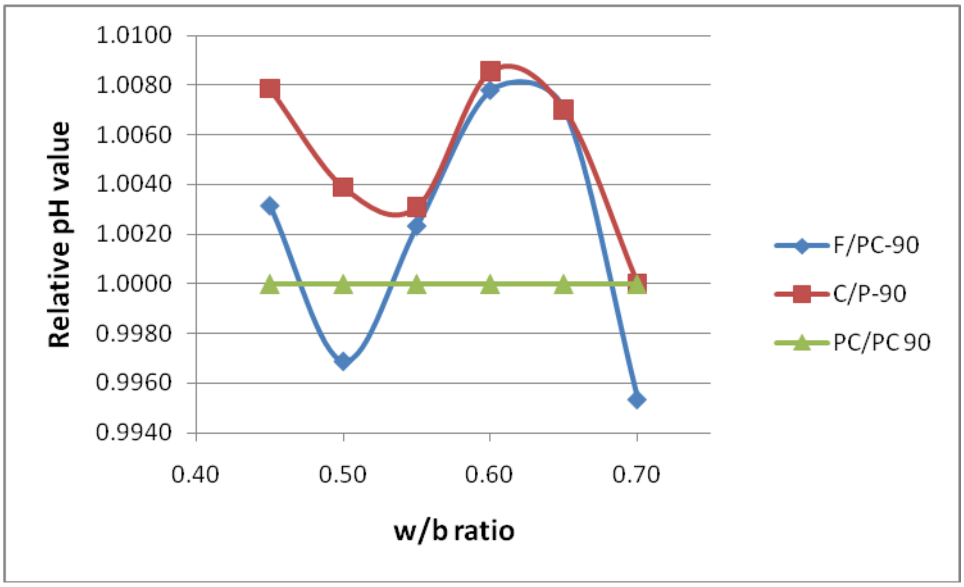

Figure 4-12: Relative pH value of concretes at 90 days

In 7 day the pH of fly ash added concretes stayed under the pH values of plain concrete due to the inactivity of fly ash in the early ages. After 28 days the pH values of fly ash added concretes started to increase and meet the reference line of plain concrete. In 90 days age the pH values of fly ash added concretes exceeded the reference line and got higher values than the values of plain concrete. However, C class fly ash added concrete had a higher pH value than the value in F class due to the higher CaO content of C class but there is always special point at w/b ratio of 0.55 where the value of pH values get closer to eachother.

Figures 3.4-3.6 show that the pH values of F and C type fly ash added concretes as well as plain concrete have pHs at 90 days smaller than those measured at earier days. This result can be expected for fly ash added concretes due to the pozzolanic reaction. However for plain concretes a continuous increase in pH is expected. For the latter concretes it was found that pH decreases from 28 days to 90 days. In order to understand this conradiction the pHs of the water in the curing pools were measured and found as 10, 9.72, 9.81 for the three pools. Those results show that the water in the pools is not lime saturated (ASTM C511). Consequently, the reduction of pH of plain concrete after 28 day can be due to leaching of lime at later ages. Furthermore, the lowest pH belongs to plain concrete at 90 days, which may be attributed to the higher leaching of plain concrete as a result of greater permeability of this concrete than those of fly ash added concretes. As it is well known pozzolans decrease the permeability of concretes.

4.5 Efficiency factor of the fly ash used in concrete

Efficiency factor of fly ash is defined as the percentage of fly ash that is considered to act like portland cement in fly ash added concretes [18]. To calculate the effciency factor the following formula can be used:

f_c= K{ [(C+kF)/W]-0.5}

f_c: compressive strength of the specimen, K: empirical parameter, C, F and W are cement, fly ash and water content in the mortar respectively (kg/m^3), and k is the efficiency factor of fly ash. Using the formula above, k value can be found easily. Afterwards, the diagrams of efficiency of fly ash, in the fly ash added concretes, were drawn for 7, 28 and 90 day ages.

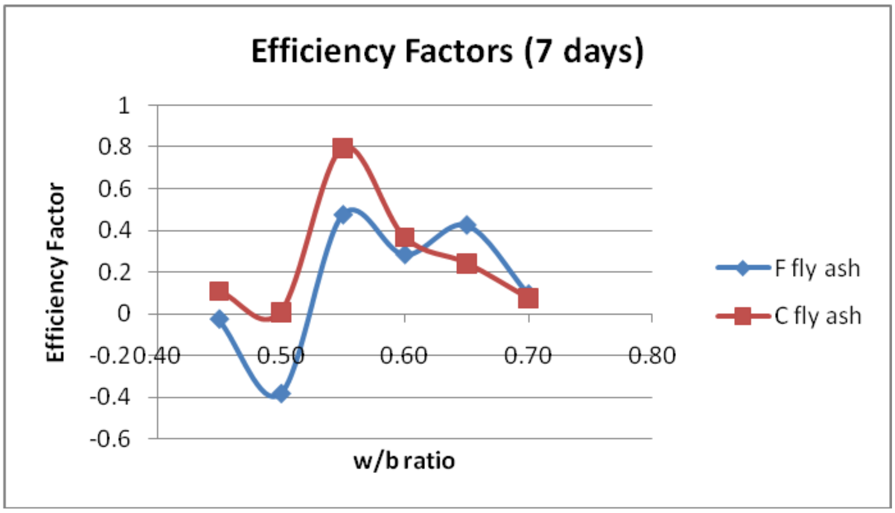

Figure 4-13: Efficiency factors of fly ashes for 7 days age

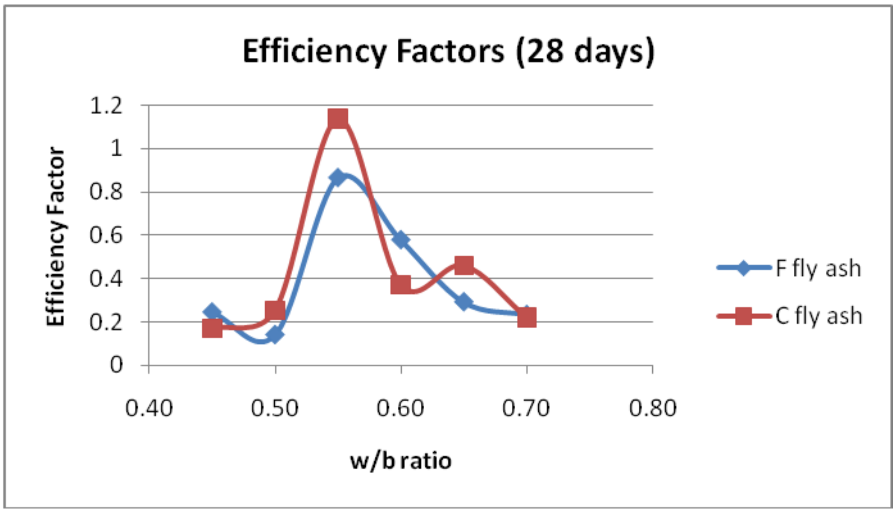

Figure 4-14: Efficiency factors of fly ashes for 28 days age

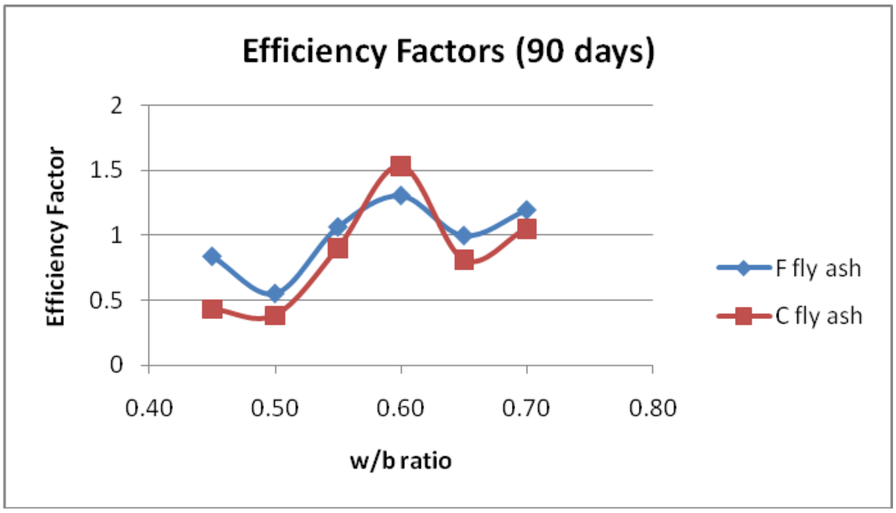

Figure 4-15: Efficiency factors of fly ashes for 90 days age

From the Figures 4-13, 4-14 and 4-15, it is clear that as the age of concrete grows, the value of efficiency factor (k) is growing as well. Although, at 7 days the vlaues are very low, it is obviuos that efficiency factor kept growing from 7 days to 28 days graduately, and the peak piont of the efficiency factor is seen at the w/b ratio of 0.55. The situation at 90 days seems similar as the value of k kept growing, but the optimum point changed from w/b ratio of 0.55 to 0.6.

4.6 Comparison between relative values and efficiency factor

To understand the behavior of fly ash added concretes with respect to the plain concrete at 7 days, Figure 4-4, Figure 4-10 and Figure 4-13 were analysed.

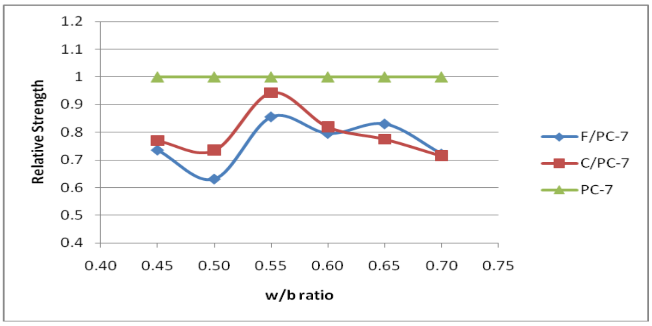

Figure 4-4: Relative strength of F class and C class fly ash added concretes in 7 days

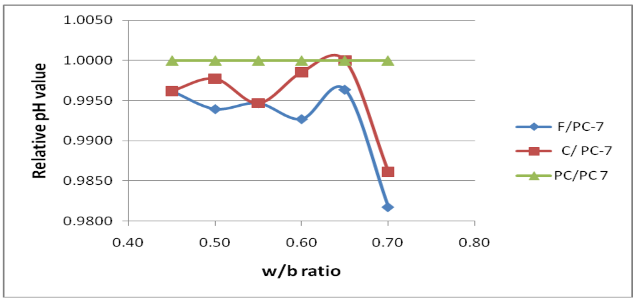

Figure 4-10: Relative pH value of concretes at 7 days

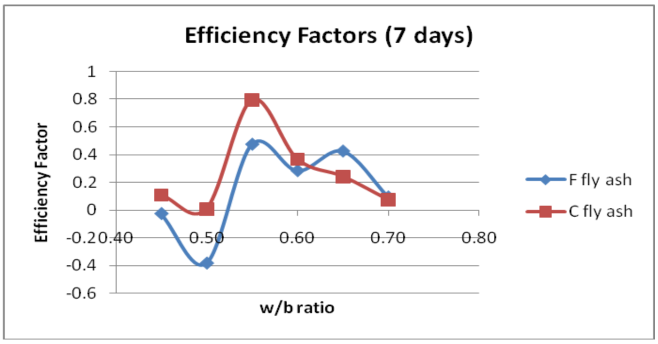

Figure 4-13: efficiency factors of fly ash for 7 days age

In the figures above, the strength and pH values of fly ash added concretes considered to be lower than the corresponding strength and pH values of plain concretes this can be explain due to the inactivity of fly ash in the first days and this can be seen in Figure 4-13 as the efficiency factor of fly ashes are very low.

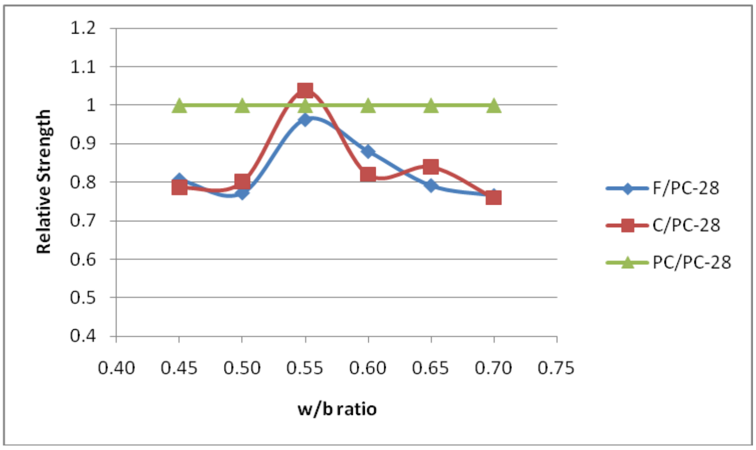

Figure 4-5: Relative strength of F and C class fly ash added concretes in 28 days

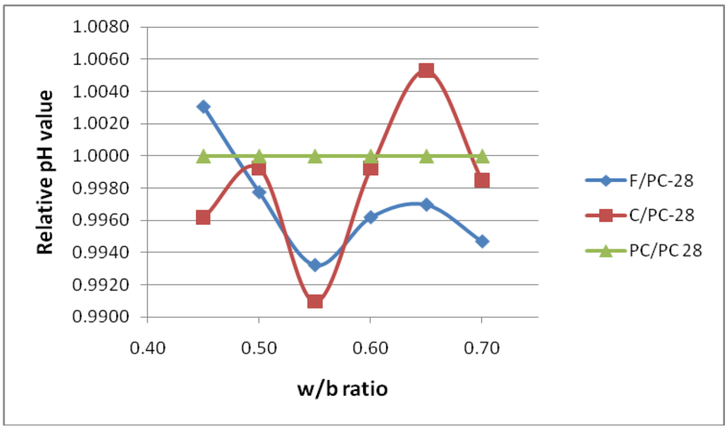

Figure 4-11: Relative pH value of concretes at 28 days

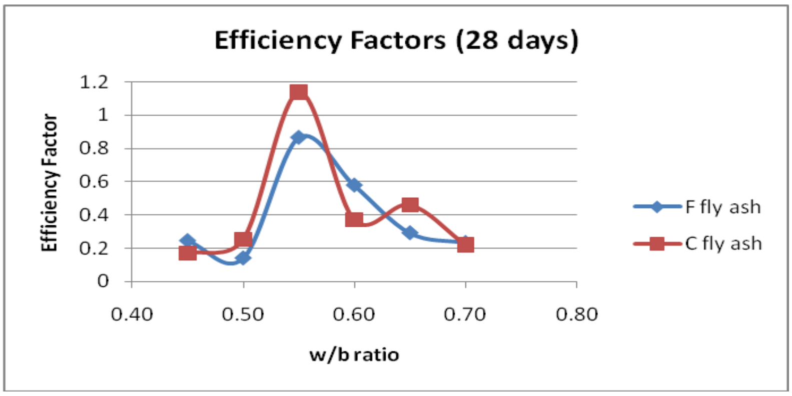

Figure 4-14: efficiency factors of fly ash for 28 days age

In Figures (4-5 and 4-11), an increase in strength and pH values of fly ash added concretes at age of 28 days with respect to those values of plain concrete. This can be explain as the fly ash started to enter the pozzolanic reaction, it is clear in Figure

4-14 efficiency factor increased, this means that a big part of fly ash started to act as cement in the mixture.

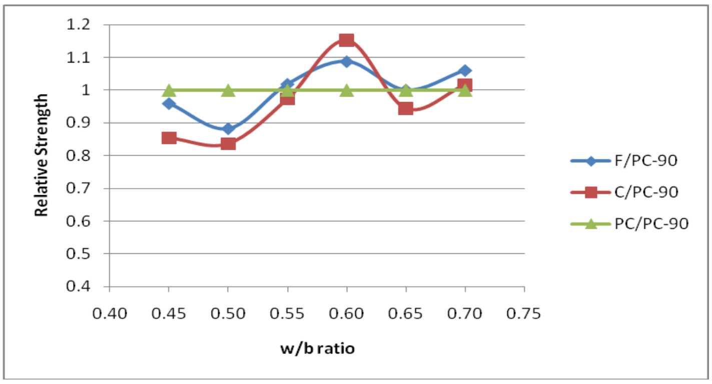

Figure 4-6: Relative strength of F class and C class fly ash added concretes in 90 days

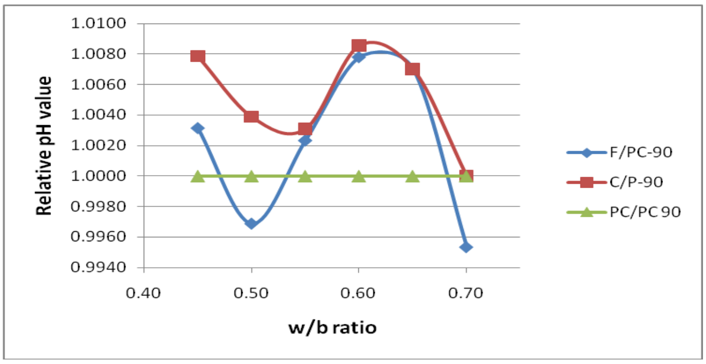

Figure 4-12: Relative pH value of concretes at 90 days

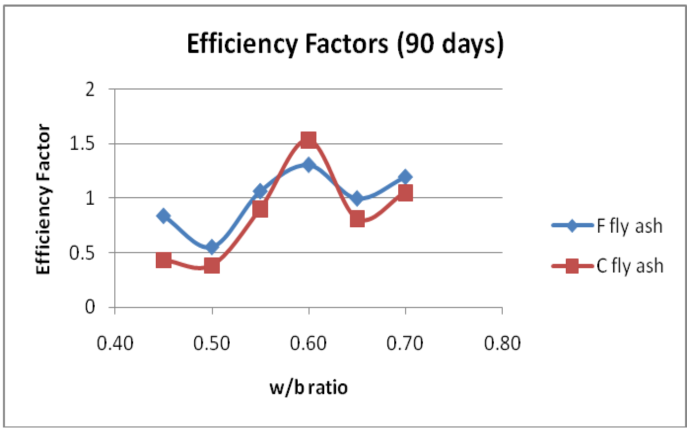

Figure 4-15: efficiency factors of fly ash for 90 days age

In Figures (4-6 and 4-12), at age of 90 days the strength and pH values of fly ash added concretes started to exceed the those values of plain concrete in most cases. This can be explain as the fly ash started to enter the pozzolanic reaction in big amounts, it is clear in Figure 4-15 efficiency factor increased to react the value of 1 or more in some cases, this means that a big part of fly ash started to act as cement in the mixture.

The compressive strength in the early ages (7 and 28 days) of fly ash added concrete is lower than the strength values of the plain concrete but between 28-90 days fly ash concretes start to gain strength till they exceed the plain concrete strength values after 90 days, similar to what lam et al. referred to in [19]. In a parallel way, The pH values in the early ages (7 and 28 days) of fly ash added concrete is lower than the pH values of the plain concrete [20], but between 28-90 days fly ash concretes start to lose alkalinity after 90 days due to the increase of pozzolanic reaction [21].

For a specific age, the strengths of the mixtures with fly ash (either F or C type) were divided by the corresponding strengths of the concretes, which are fly ash free, for the same w/c ratios; hence relative strengths were obtained.

There are two effects here; one is accelerating of hydration reaction due to the increase in water content by increasing w/c ratio. As a result of higher hydration reaction rate more lime will be generated. However for high w/c ratios, since water content increases, the Ca^{++} ion concentration in pore solution decreases. The latter situation causes a kind of dilution of Ca^{++} ions, which may reduce the pozzolanic reaction of fly ash [22]. It seems that there is an optimum w/c ratio for the highest pozzolanic reaction, which is 0.55 for both fly ashes tested and for both 7 and 28 days. However, the optimum w/c ratio is shifted to 0.60 for both fly ashes at the age of 90 days. At this age, the strengths of fly ash added concretes exceed those of PC concretes without fly ash.

In general, an optimum point is figured in all the diagrams above where the w/b ratio is 0.55, in 7 and 28 days it seems to be maximum for the strength values of fly ash added concretes but at the same time it is minimum for pH values similar, this can be due to the pozzolanic reaction when fly ash reacts with $Ca(OH)_2$ so the pH goes low but at the same time it results in producing more C-S-H gel ti increase the stregnth. At 90 days the situation is different, as both values of relative strength and relative pH are maximum but at the point of w/b ratio of 0.6, this can be explain as the fly ash kept reacting to produce C-S-H gel but at the same time the water content of high w/b ratio mixtures is decreasing and this makes the the Ca^{++} ion concentration in pore solution increases.

5. CONCLUSIONS

- Compression strength of plain concretes is higher than the compression strength of fly ash added concretes of 7 days for all w/b ratios. For low w/b ratios (lower than 0.6), the strength of C class fly ash added concretes exceeded those of F class fly ash added concretes. However, at higher w/b ratios two type cocnretes have almost similar strengthes.

- At 28 days, plain concretes show the highest strength for all w/b ratios, however, for w/b ratio of 0.55, all concretes including fly ash added ones have almost similar strength. For fly ash added concretes, it can be said that there is no definite difference between the strengthes with varying w/b ratios.

- At 90 days, the plain concretes show the highest strength for w/b $\leq$ 0.55, F type fly ash added concretes follow it and C type fly ash added concretes have the lowest strength. However, for w/b $>$ 0.55 there is no significant tendency of results with w/b.

- Relative strength of cocnretes were calculated by dividing every value fly ash added concretes strength with the corresponding values of plain concretes. At 7 days, for fly ash added concretes w/b ratio of 0.55 gives the highest relative strength than the other w/b ratios, where the C type fly ash concretes have the highest relative strength. At 28 days, a similar manner, like the one at 7 days, is observed and the relative strength of C type fly ash added concretes of w/b 0.55 seems to be higher than both F ash added concretes and plain ones at the same point. At 90 days, for fly ash added concretes w/b ratio of 0.60 gives the highest relative strength than the other w/b ratios, where the C type fly ash concretes have the highest relative strength and both fly ash added concretes of both types (C type and F type) are higher than the value of plain concretes.

- It seems that the point of w/b ratio is an optimum point for the maximum strength of fly ash added cocnretes at 7 and 28 days, but at 90 days this point apears to be at w/b ratio of 0.60.

- It was found that for w/b ratio smaller than 0.60 and at later ages (90 days) the amount of extracted water was not enough to carry out pH measurement.

- pH values measured by pore solution method are about 1.04 times greater than those of powder solution method for the w/b ratios between 0.60-0.70.

- At 7 days, the highest pH belongs to the plain concretes. C type fly ash added concretes follow palin ones, and F type fly ash added concretes have the lowest pH value. At 28 days, the pH values of all concretes do not have a specific manner and seem to be close to each others. At 90 days, C type fly ash added concretes have the highest pH values for w/b > 0.50, plain concretes have the lowest pH except w/b ratio of 0.70. It seems that the pH values of all concretes decreases from 28 days to 90 days. This behavior is expected for the fly ash added concretes due to the pozzolanic reaction. On the other hand, the decrease observed in plain concretes at 90 days can be due to the leaching of lime in these concretes because of low lime content of the curing pools.

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